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Correlation analysis in the chemistry of free radicals

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Abstract. Published data now available on the use of correlation analysis in free-radical chemistry are discussed systematically. The scales of 'radical' σ-constants of substituents proposed previously are analysed. It is shown that none of them is applicable as a general scale because almost in all cases, it is impossible to separate correctly the proper radical and polar contributions to the overall effect of substituents. A new approach to the quantitative estimation of the relationship between the structure and reactivity of molecules in free-radical processes called r^{-2}-analysis is proposed. The bibliography includes 238 references.

I. Introduction

Correlation analysis is a widely used mathematical formalisation of the chemical similarity principle.

The foundations of the analysis were laid by Hammett, who discovered a correlation between the rate constants (k) or equilibrium constants (K) of reactions involving benzene derivatives and the ionisation constants of benzoic acids [1]

$$\log\frac{k_X}{k_H} = \rho\log\frac{K_X}{K_H} = \rho\sigma,$$

where the subscripts X and H refer to substituted and unsubstituted derivatives and ρ is the reaction constant for the given series. The reaction series of dissociation of benzoic acids in aqueous solutions at 25 °C was chosen as the reference series, described by $\rho = 1$, and the ratio

$$\log\frac{K_X}{K_H},$$

was introduced as the σ-constant, reflecting the influence of the substituent X in a set of similar reaction series. This empirical approach, which is also known as $\sigma\rho$-analysis, became one of the first quantitative methods for describing the structure – reactivity relationship for compounds and has served as the basis for the subsequent development of the general formal theory of the influence of substituents.

The principles of linear free energy (LFE) and polylinearity (PL) provide the physical grounds for this approach, according to which the increment of the Gibbs energy change (ΔG) in a reaction or of the activation energy caused by the introduction of a substituent is represented as the additive sum

$$\delta\Delta G = \delta\Delta G_I + \delta\Delta G_S + \delta\Delta G_R,$$

each of the terms reflecting a particular type of substituent effects, namely, inductive (I), steric (S) or resonance (R) effect. The multitude of inductive, steric and resonance constants determined from diverse experimental sources, together with some specific constants (for example, 'phosphorus' or 'silicon' constants) form dozens of scales which are widely used to describe the influence of substituents on the reactivity at the group level of additivity.

Various aspects of the determination and versatile practical application of steric and inductive constants of groups and the concept of electronegativity tightly connected to them have been described in detail in our previous reviews.[2–5] It should only be noted that modern correlation analysis has long overstepped the limits of a purely empirical approach. The group constants of substituents have provided the experimental basis for the physical interpretation and for the development of various quantitative models describing the steric and electronic effects.

Certainly, some key problems of the formal theory of interaction and correlation analysis are still to be ultimately solved. For example, the nature of the inductive effect and the mechanism of its transfer remain one of the most debatable and topical problems of physical chemistry [2] (the state-of-the-art in this line of research has been discussed comprehensively in recent review publications [5–8]). Nevertheless, it can be stated with confidence that the theoretical grounds of modern correlation analysis provide in general a clear picture and give good grounds for the extensive use of the substituent constants for description of the structure – property relationships in the chemistry of organic and heteroorganic compounds. Perhaps, the only field of chemistry in which the use of correlation analysis has not yet provided good results is free-radical chemistry. The application of LFE and PL principles in this field of chemistry is still limited to a rather narrow range of compounds (mainly, aromatics).

In this review, the current state of the use of correlation analysis for radical reactions is considered for the first time. In addition, we thought it necessary to present the generalising results obtained by the new approach to the estimation of the structure – reactivity relationship in free-radical reactions which we have developed and called 'r^{-2} analysis'.

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II. Correlation analysis for reactions involving free radicals

1. Methods for the description of the effects of substituents in homolytic processes based on kinetic parameters. $\sigma^{\cdot}$-Scales

Despite the fact that the applicability of the Hammett equation to homolytic processes is sometimes debated,[9] there exist quite a few examples of successful use of various polar constants for the description of free-radical reactions.[10–28]

In addition to the proper Hammett σ-constants,[18–29] which reflect the overall effect of substituents in aromatic systems, so-called dual σ^+ and σ^- parameters of substituents, which imply direct polar (mesomeric) interaction of $^+$M or $^-$M substituents with the reaction centre, are also actively used in the analysis of homolytic processes.

The scale of σ^+-constants proposed by Brown and Okamoto,[30] which is based on the rates of solvolysis of *para*- and *meta*-substituted cumyl chlorides, is believed to be more adequate in describing the properties of aromatic radicals than the scale of Hammett σ-constants.[31] In our opinion, the use of σ^+-constants is really more effective as far as the properties of radical cations are concerned but this is not that obvious for neutral radicals. Nevertheless, radical bromination of substituted toluenes with bromine,[24] *N*-bromosuccinimide [24] and bromotrichloromethane [32] as well as the quantitative interpretation of abstraction of a hydrogen atom by alkoxy radicals,[11,12,33] chlorine atoms,[34] and peroxy radicals [34] have become classical examples of successful use of the σ^+ constants in free-radical chemistry. Experimental results obtained by one of the authors of this review have confirmed the exceptionally high efficiency of the σ^+ constants in correlations with single-electron reduction potentials of various aromatic molecules and radicals.[35–40]

Other researchers [18,41] have also considered the Brown–Okamoto scale to be the most suitable scale for the description of properties of free radicals; it is the scale of σ^+ constants that has served as the base for the introduction of several specific radical constants of substituents $\sigma^{\cdot}$ (they will be considered in detail in the subsequent sections of this review).

The σ^--constants found from the pK values for ionisation of substituted anilines, *N*,*N*-dimethylanilines and phenols [42,43] have also been used successfully to describe a number of radical processes.[29,44] However, polar constants are finding fairly limited application in free-radical chemistry. The scope of application of particular scales to the description of properties of free radicals remains obscure, identification of statistically significant correlations in each successful case being rather a matter of luck than of a systematic approach. Additional difficulties arise when the correlation analysis technique is employed to describe the properties of non-aromatic free radicals.

The main problem in the quantitative estimation of the effects of substituents in homolytic processes is, undoubtedly, the necessity of adequate description of their ability to delocalise the unpaired electron. Currently, this is one of the most topical and ambiguous problems in free-radical chemistry (see, for example, a monograph [45] and references therein).

There is a common opinion that both donors and acceptors are capable of stabilising a radical centre;[45] this is often used as an argument in favour of the introduction of special radical $\sigma^{\cdot}$ constants of substituents, which are expected to describe quantitatively the ability of substituents to delocalise spin density. The methods of determination of $\sigma^{\cdot}$-constants can be classified into three main types. The first type includes methods based on the use of kinetic parameters of homolytic processes; the second type comprises physicochemical methods which provide direct information on the spin density distribution in radicals; and thermodynamic approaches operating with energy characteristics belong to the third type. Below we consider the existing approaches in accordance with this classification.

The methods based on the kinetic parameters of homolytic processes are used most widely in determining the $\sigma^{\cdot}$-constants of substituents and are modifications of the classical correlation analysis, based on the use of the extended Hammett equation

$$\log\frac{k}{k_0} = \rho_1\sigma^{X} + \rho_2\sigma^{\cdot}. \qquad (1)$$

The essence of this approach is to separate the contribution of the proper radical stabilisation ($\sigma^{\cdot}$) from the polar effect (σ^{X}); hence, it requires selecting a model reaction series in which the latter contribution would be small and could be determined reliably in terms of polar constants. The most widely used reactions involving free radicals include electron transfer, free-radical transfer of a hydrogen atom and radical addition.

The kinetic approach to the description of the effects of substituents in radical reactions was first employed by Alfrey and Price [46] in a study of the reactivity of vinylic monomers in copolymerisation. The researchers [46] did not use the classical logarithmic form of Eqn (1); however, the capacity of substituents for stabilisation of radicals was estimated quantitatively for the first time in terms of group constants Q, whereas the polar component was taken into account by the parameter e (the Q constants are given in Table 1)

$$\frac{k_1}{k_2} = \frac{Q_1}{Q_2}\exp\left[-e_1(e_1 - e_2)\right]. \qquad (2)$$

A substantial disadvantage of this approach is the fact that the calculation of Q is based on the analysis of a set of data on copolymerisation, and introduction of new individual values requires a consistent procedure for recalculation of the whole array of Q.

Walling *et al.*[59] have critisised the theoretical substantiation of the Alfrey–Price approach, which ignores the possibility of resonance stabilisation of a radical transition state.

Later, the group parameters E_R have been introduced using the relative reactivity of monomers ($1/r$) in the radical copolymerisation of aryl-substituted methacrylates [47,48,60]

$$\log\frac{1}{r} = \rho\sigma + \gamma E_R\,, \qquad (3)$$

where the γ coefficient was taken to be 1, and the parameter E_R was interpreted as the resonance component of the substituent effect in free-radical processes. Subsequently,[49] this approach was subjected to severe criticism, the legitimacy of the E_R and γ values being prejudiced. The researchers [49] believed that the nature of E_R is rather complex; therefore they proposed adjusted values, E_R^n, free from the contribution of heterolytic resonance (see Table 1).

A similar scale of resonance constants E_D has been developed to describe the effects of *para*-substituents in the addition of trichloromethyl radical to substituted styrenes [53]

$$\log\frac{k_p}{k_H} = \rho\sigma_p^{+}(\rho\sigma_p) + E_D\,; \qquad (4)$$

in this case, the polar effect was taken into account by both the Brown–Okamoto constants and the Hammett σ_p-constants. Correspondingly, two sets of E_D parameters for *para*-substituents (MeO, Cl, CN, NO_2) in styrenes were obtained [$E_D(\sigma)$ and $E_D(\sigma^+)$ in Table 1]. The E_D constants of these substituents found using the σ^+ parameters are in good agreement with the Alfrey–Price Q constants.

A similar approach was used [54] to develop the τ scale, which reflects the conjugation effects in radical arylation of substituted benzenes

$$\log\frac{k_p}{k} = \rho\sigma_p + \tau_p\,, \qquad (5)$$

where k_p are the rate constants for the arylation into the *para*-position expressed in terms of the Hammett constants of *para*-substituents (σ_p) and the group parameters τ_p, which reflect the additional delocalisation effects of *para*-substituents. The ρ-constant appearing in Eqn (5) was determined on the basis of a similar reaction series of *meta*-arylation, the influence of substituents

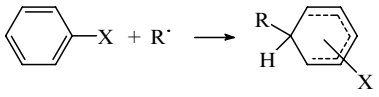
Table 1. Constants characterising the radical-stabilisation properties of substituents (data of kinetic studies).

Substituent	log$Q$	$E_R(p)$	$E_R(m)$	E_R^n	$E_D(\sigma)$	$E_D(\sigma^+)$	τ_p	τ_o	$\sigma^{\cdot}_{FM}$	$\sigma^{\cdot}_J$	$\frac{\lvert\sigma^{\pm}-\sigma\rvert}{n}$	$\sigma^{\cdot}_C(p)$	$\sigma^{\cdot}_C(m)$	$\sigma^{\cdot}_{JJ}(p)$	$\sigma^{\cdot}_{JJ}(m)$
	see [a]	see [b]	see [b]	see [c]	see [d]	see [d]	see [e]	see [e]	see [f]	see [g]	see [h]	see [i]	see [i]	see [j]	see [j]
H	0.00	0.00	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.00	0.00	0.00	0.00
Me	0.04	0.03	–	−0.020	0.16	0.11	0.09	0.50	−0.02	0.38(0.39)	0.170	0.11	−0.02(0.03)	0.15	0.00
OMe	0.13	0.11	–	−0.008	0.40	0.19	0.14	–	−0.12	0.31(0.42)	0.250	0.24	−0.02	0.23	0.10
NO_2	0.21	0.41	0.35	0.410	0.27	0.27	0.90	0.88	0.27	0.73(0.76)	0.440	0.57	−0.11	0.36	0.001
CN	0.27	0.24	–	0.230	0.33	0.32	–	–	0.34	(0.41)	0.260	0.46	−0.12	0.42	0.11
F	–	–	–	–	–	–	–	–	−0.25	0.07(0.12)	0.065	−0.08	−0.05	−0.02	0.03
Cl	0.01	0.10	0.08	0.062	0.12	0.07	0.16	0.48	0.08	0.06(0.18)	0.065	0.12	−0.04	0.22	−0.05
Br	0.04	0.12	–	0.072	–	–	–	–	0.17	(0.20)	0.055	0.13	–	0.23	0.12
I	0.07	0.12	–	0.037	–	–	–	–	0.16	–	0.075	0.41	0.10	–	–
OH	–	0.21	–	–	–	–	–	0.57	–	–	–	–	–	–	–
C(O)Me	–	–	–	0.240	–	–	–	–	0.53	–	–	–	–	0.54	–
$P(O)(OEt)_2$	–	–	–	–	–	–	–	–	–	–	–	0.18	−0.11	–	–
$P(S)(OEt)_2$	–	–	–	–	–	–	–	–	–	–	–	0.29	−0.06	–	–
Ph	–	–	–	–	–	–	–	–	0.12	0.39(0.42)	0.230	0.46	–	0.47	–
SMe	–	–	–	–	–	–	–	–	–	(0.49)	–	0.43	−0.03	0.62	–
SPh	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
CF_3	–	–	–	–	–	–	–	–	–	–	–	0.08	−0.07	−0.01	−0.07
OPh	–	0.13	–	−0.147	–	–	–	–	–	–	–	–	–	–	–
CO_2Et	–	–	–	–	–	–	–	–	–	–	–	0.39	–	–	–
CO_2Me	–	–	–	–	–	–	–	–	–	–	–	0.35	–	0.33	0.10
C(O)Ph	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Bu^t	–	0.03	–	0.014	–	–	–	–	–	–	–	0.13	–	0.26	0.11
Et	–	–	–	–	–	–	–	–	–	–	–	–	–	0.15	–
Pr^i	–	0.03	–	0.034	–	–	–	–	–	–	–	–	–	–	–
SOMe	–	–	–	–	–	–	–	–	–	–	–	0.18	0.01	0.50	–
SC(O)Me	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
S(O)OMe	–	–	–	–	–	–	–	–	–	–	–	0.18	−0.07	0.38	–
SO_2Ph	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
S(O)Ph	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
SO_3Me	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
OC(O)Me	–	–	–	–	–	–	–	–	–	–	–	–	–	−0.11	−0.10
OC(O)Ph	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
N = NPh	–	–	–	–	–	–	0.90	–	0.33	–	–	1.08	–	–	–
NH_2	–	–	–	–	–	–	–	–	–	–	–	0.69	–	–	–
NMe_2	–	0.24	–	−0.110	–	–	–	–	–	–	0.535	0.90	–	1.00	–
$SiMe_3$	–	–	–	–	–	–	–	–	–	–	–	0.17	–	0.31	–
$CH = CH_2$	–	–	–	–	–	–	–	–	–	–	–	0.67	–	–	–

Note. The values which vary in original publications are given in parentheses.

[a] From Ref. 46; [b] from Refs 47, 48; [c] from Refs 49 – 52; [d] from Ref. 53; [e] from Ref. 54; [f] from Ref. 55; [g] from Refs 50 – 52; [h] from Ref. 56; [i] from Ref. 57; [j] from Ref. 58.

being entirely ascribed to the polar interaction. The parameters τ_o for *ortho*-substitution were introduced by a similar procedure. The 4-$XC_6H_4\dot{C}H_2$ radicals, where X = H, NO_2, Cl, Me, MeO, were investigated (regardless the nature of the attacking agent); in this case, the τ_p and τ_o constants decreased in the series $PhNO_2 \gg$ PhCl, PhOMe > PhMe (see Table 1). This model series has an important advantage: the measured kinetic parameters vary over a broad range due to the direct conjugation of para-substituents with a cyclohexadienyl radical.



However, it cannot be ruled out that, within the framework of the given reaction series, fairly reactive phenyl radicals would be involved with high probability in side homolytic properties.

The methodology of the above approaches is evidently similar to that used in the classical equations of correlation analysis, which determine the inductive and resonance constituents of the polar effect of substituents in terms of Taft,[42,61–63] Exner,[64–66] Yukawa–Tsuno,[67,68] Swain–Lupton,[69] Dewar–Grisdale,[70] Charton[71] and Palm[72,73] approaches. In all the studies described above, except for the study by Alfrey and Price,[46] the researchers dealt only with aromatic systems. Therefore, the radical constants τ, E_R and E_D are believed to contain a component due to the polar effect.

Fisher *et al.*[55,74,75] used radical bromination of 4-substituted 3-cyanotoluenes with *N*-bromosuccinimide as the model reaction to determine the 'extra-resonance' (this name was proposed by the authors), *i.e.*, the proper radical contribution (the polar contribution is minimised). When considering the possible canonical forms of the transition state of hydrogen abstraction *via* the reaction

$$YH + Z^{\cdot} \longrightarrow \underset{\mathbf{1a}}{\left[\dot{Y}\,\dot{H}\,\dot{Z}\right.} \longleftrightarrow \underset{\mathbf{1b}}{Y^{+}\,\dot{H}\,Z^{-}} \longleftrightarrow \underset{\mathbf{1c}}{\left.Y^{-}\,\dot{H}\,Z^{+}\right]},$$

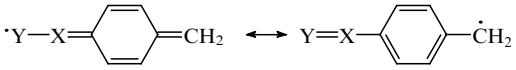
the researchers suggested that the high electronegativity of the attacking bromine atom Z precludes a substantial contribution of structure **1c**. In order to destabilise the polar form **1b** to decrease its contribution, the electron-withdrawing CN group was introduced in the *meta*-position relative to the methyl group (substrate YH) of the substituted toluene. The radical intermediate **1a** is stabilised additionally due to direct resonance. Assuming that the polar effects in the model system were thus minimised, Fisher *et al.*[55,74,75] proposed a scale of $\sigma^{\cdot}$ radical constants within the framework of a two-parameter equation including the Brown–Okamoto constant σ^{+}

$$\log\frac{k}{k_0} = \rho\sigma^{+} + \sigma^{\cdot}, \qquad (6)$$

in which the parameter ρ was determined on the basis of a similar reaction series of 4-substituted toluenes.

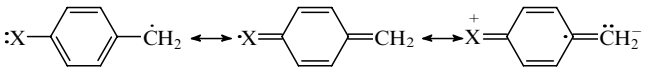
Fisher and Meierhoefer[55] did not use a series of *meta*-substituted toluenes as the standard for determining ρ on the ground that the corresponding parameter in Eqn (6) reflects, in their opinion, both the resonance and inductive polar effects. Thus, the differences between the effects of substituents in the free radical bromination of monosubstituted and 3-cyano-4-substituted toluenes by *N*-bromosuccinimide were attributed to the stabilisation of the structure **1a**; they were proposed as characteristics of the radical effects of *para*-substituents. In accordance with the results of this study, the ability of substituents to stabilise free radicals increases in the series F < OMe < Me < H < Cl < Ph < I < Br < NO_2 < N=NPh < CN < Ac, the $\sigma^{\cdot}$ constants for F and MeO being negative [$\sigma^{\cdot}$(F) = −0.25, $\sigma^{\cdot}$(MeO) = −0.12], which implies that these groups destabilise the radical reaction center (see Table 1).[55]

Meanwhile, it is obvious that the resonance stabilisatoion of substituted benzyl radicals by electron-withdrawing substituents (structures **2a** and **2b**) is similar to resonance delocalisation of the negative charge. This accounts for the most pronounced radical-stabilisation properties of substituents such as Ac, CN, N=NPh and NO_2, which also exhibit a negative mesomeric effect.



2a **2b**

In the case of stabilisation of the benzyl radical by the donor mesomeric effect of some substituents such as halogens (except for F), the researchers cited[55] discussed the formation of three contributing structures **2c**, **2d** and **2e**.



2c **2d** **2e**

Structure **2e** is characterised by substantial charge separation, which makes it energetically less favourable. The electrically neutral structure **2d** implies delocalisation of the unpaired electron because it has been added to the electron octet of the X atom. As Tsuno *et al.*[68] rightly noted, elements of Period II, O and F, are incapable of this type of interaction, which accounts for the negative values of the corresponding radical constants.

The presence of negative $\sigma^{\cdot}$ values in the Fisher–Meierhoefer scale hampers its quantitative comparison with other known scales, in most of which the radical constants can be only positive, implying that the radical reaction centres are stabilised by both donors and acceptors. It should also be noted that in the model system of disubstituted toluenes proposed, the possibility of resonance effect of *para*-substituents is retained, despite the minimisation of polar effects.

The search for standard reaction series with a clear-cut radical character of the transition state, which rules out a noticeable influence of polar interactions, has led Jackson *et al.*[50,51,56,76,77] to consideration of the thermal dissociation of dibenzylmercury derivatives in solution.

$$ArCH_2HgCH_2Ar \longrightarrow Ar\dot{C}H_2 + \dot{H}gCH_2Ar$$

$$\dot{H}gCH_2Ar \longrightarrow Hg + Ar\dot{C}H_2\,.$$

It was found that homolysis occurs in two stages. The first, rate-determining stage is generation of benzyl and benzylmercurio radicals;[52,78,79] it was suggested that in the transition state, one C–Hg bond has been cleaved almost completely, which corresponds to the formation of a nearly free benzyl radical.

The conventional $\sigma\rho$-analysis, which makes use of the first-order rate constants for the reaction under consideration and the Hammett σ-constants (subsequently, the σ^0 parameters were used), identified a linear correlation for *meta*-derivatives, whereas *para*-substituents of both electron-donating and electron-withdrawing nature accelerate homolysis, due to an additional stabilisation of benzyl radicals. In the equation

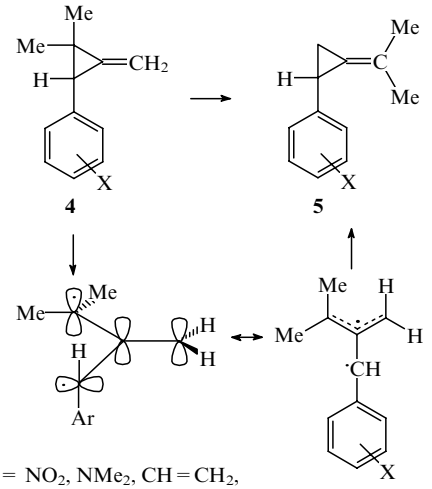
$$\log\frac{k}{k_0} = \rho\sigma + \rho^{\cdot}\sigma^{\cdot} \qquad (7)$$

resulting from the correlation procedure, the parameter $\rho^{\cdot}$ was taken to be unity for reactions giving rise to free benzyl radicals in the rate-determining step. In terms of the regression analysis performed, the constants which were later designated by $\sigma_J^{\cdot}$ (see Ref. 45) and which reflect the stabilising effect of substituents in the *para*-position of the benzyl radicals were determined from the deviations from the *meta*-correlation (see Table 1). The $\sigma_J^{\cdot}$ values were found to be in good agreement with the Q, τ, E_D and E_R scales (the correlation coefficients r varied from 0.83 to 0.92); as regards the Fisher–Meierhoefer constant ($\sigma_{FM}^{\cdot}$), only some qualitative correspondence was found in this case (r = 0.63).

It has been proposed[56] to use the $|\sigma^{\pm} - \sigma|/n$ scale, where $\sigma^{\pm}$ is the σ^{+} or σ^{-} constant, as a measure of radical stabilisation; for substituents containing a lone electron pair n = 2, while for groups with a multiple bond or any other π-system, n = 1. This

scale correlates well with the $\sigma_J^{\cdot}$ values. As drawbacks of this approach, the authors note the difficulty of preparing a broad range of dibenzylmercury derivatives and the limited solubility of these compounds in octanol, used as the reaction medium.

An attempt to select a perfect free-radical transition state is also the central point in Creary's approach,[57,80–84] in which thermal rearrangement of 3-aryl-2,2-dimethylmethylenecyclopropanes **4** has been used as a standard reaction series to introduce the scale of radical constants $\sigma_C^{\cdot}$.



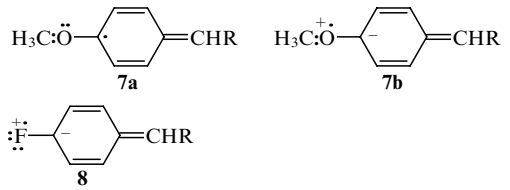
X = NO_2, NMe_2, $CH=CH_2$, $C(Me)=CH_2$, Ph, cyclo-C_3H_5, CH_2SiMe_3, $SiMe_3$, $SnMe_3$, HgCl, $B(OCH_2CH_2O)$.

The transition state of the rearrangement is of biradical nature; this has been confirmed in a series of studies.[85–94] Proceeding from the assumption that the biradical nature of the transition state rules out the possibility of substantial charge separation in it, Creary suggested using the logarithm of the relative rate constant for the reaction, k_{rel}, as a measure for the ability of substituents to stabilise the benzylic radical centre

$$\sigma_C^{\cdot} = \log k_{rel} . \quad (8)$$

The kinetic parameters of thermal rearrangement of 2-aryl-3,3-dimethylmethylenecyclopropanes **4** into 2-arylisopropylidenecyclopropanes **5** can be easily determined by gas chromatography or NMR; this permits determination of radical constants for *meta*- and *para*-substituents of the aromatic ring within the framework of this approach. It is also possible to evaluate the stabilising influence on the radical centre of heteroorganic substituents.[45]

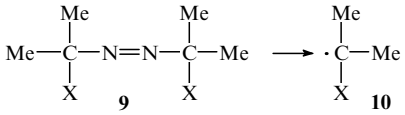
It was found [57,84] that electronegative substituents in the *meta*-position retard the rearrangement, which might point to an electron-deficient character of the biradical transition state. Most *para*-substituents, both electron-donating and electron-withdrawing ones have positive values of $\sigma_C^{\cdot}$ constants. An exception is F, for which $\sigma_C^{\cdot} = -0.08$ (see Table 1); this was explained by the destabilising influence of F caused by the enhanced inductive effect. The influence of the *para*-methoxy group was regarded as stabilisation ($\sigma_C^{\cdot} = 0.24$), caused by the contribution of the canonical forms **7a**,**b**.



A similar structure for the *para*-fluorine-substituted system appears less favourable because of the high electronegativity of fluorine. From the molecular-orbital standpoint, the stabilising effect of the *para*-methoxy group can be due to the interaction of the radical centre with the filled non-bonding orbital of oxygen; however, the low energy of the filled 2*p* orbital of fluorine precludes manifestation of the effects of this type.

As has been noted in a monograph,[45] synthesis of a broad range of methylenecyclopropanes **4** is quite difficult; therefore, the reaction series proposed by Creary has no advantages in this respect over thermal dissociation of mercury dibenzyl derivatives. In addition, it is not quite clear to what extent the centre in the transition state **6** is a radical centre. Nevertheless, this approach has been successfully developed; it was shown in a recent publication [94] that the introduction of nitrogen-containing substituents into the *para*-position of the substrate **4** provides considerable radical stabilisation. Moreover, some substituents, for example, $CH=NNMe_2$, $N=NPh$, $N=N(O)Bu^t$ and $CH=N(O)Bu^t$ ($\sigma_C^{\cdot}$ = 0.92, 1.08, 1.08 and 1.13, respectively), displayed extraordinary radical-stabilisation capacity; they were called super-stabilisers.

A free-radical transition state in aliphatic systems [45,95–100] has been modelled by pyrolysis of substituted azopropanes **9**.

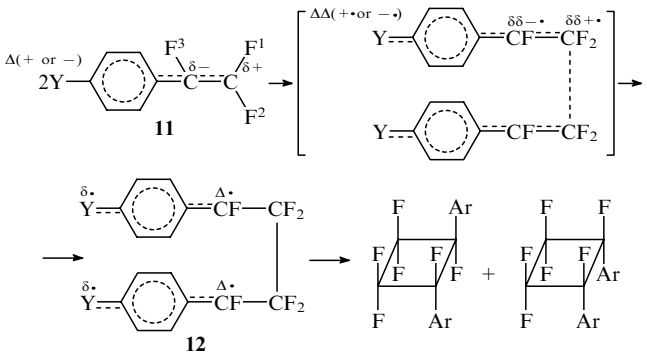


According to the researcher's assumption, this reaction series is characterised by slight steric and inductive interactions; therefore, the pronounced difference between the reaction rates (the range of variation of the rate constants is 10^9) is interpreted as being due exclusively to resonance stabilisation. Later, the kinetic characteristics of pyrolysis of the azopropanes **9** were found to be well correlated with the Creary radical constants $\sigma_C^{\cdot}$, despite the substantial difference between the structures of the radical substrates **6** and **10** and the fact that the extents of influence of substituents on the radical centres are difficult to compare.[83]

The series of model aryl-substituted azoalkanes has been markedly extended [101] by the inclusion of polycyclic azoalkane derivatives,[102] symmetrical azopropanes,[103,104] azoethanes,[105,106] azomethanes,[98] azoneopentanes [107] and 3,5-diaryl-1-pyrazolines,[98,108] for which the kinetic parameters of pyrolysis have been found. It is worth mentioning that, only in terms of two-parameter correlations including polar constants σ, was it possible to attain satisfactory relationships between the experimental relative rate constants for the thermolysis of azo derivatives and the corresponding Creary parameters $\sigma_C^{\cdot}$.[84]

The equilibrium constant of the dissociation of substituted hexaarylethanes to triarylmethyl radicals has been used successfully as a measure of radical-stabilising capacity of substituents.[109]

An association reaction, namely, thermal [2+2]-cycloaddition of substituted α,β,β-trifluorostyrenes **11** [58] has been used as a model series for determination of spin-delocalisation group constants $\sigma_{JJ}^{\cdot}$ (see Table 1).



An advantage of this model reaction is that no side radical processes are involved. In addition, charge distribution in the transition state **12** is symmetric, which eliminates additional polar effects. Study of the kinetics of this reaction gave a two-parameter correlation equation

$$\log\frac{k_Y}{k_H} = \rho_{mb}\sigma_{mb} + \rho^{\cdot}\sigma^{\cdot}_{JJ}, \quad (9)$$

which was employed for the introduction of spin-delocalisation constants of substituents $\sigma^{\cdot}_{JJ}$. The σ_{mb} parameter in Eqn (9) is identical to the group constant proposed previously, which is determined on the basis of fluorine chemical shifts in the ^{19}F NMR spectra of compounds **11**.[58,110–113] The mb (multiple bond) subscript reflects the hypothetical additional repulsive component of interaction between the double bond and the electron lone pair or π-electrons in the Y substituent in the compound **11** (Jiang *et al.*[113] consider this to be a fundamental feature distinguishing the scale of σ_{mb} constants from the Brown–Okamoto σ^+ constants). Equation (9) provided the possibility of determining the $\sigma^{\cdot}_{JJ}$ constants for 32 substituents (see Table 1) at five different temperatures; this allowed the researchers to verify the adequacy of the correlation parameters proposed and to introduce an averaged scale.

By the use of the $\sigma^{\cdot}_{JJ}$ scale, together with the σ^+ parameters, the kinetic data underlying other scales of $\sigma^{\cdot}$ radical constants have been reproduced with rather high accuracy within the framework of a two-parameter equation. Assuming that the $\sigma^{\cdot}_{JJ}$ parameters reflect the real ability of substituents to delocalise spin density, Dust and Arnold[114] used the ratio of the coefficients of the two-parameter equations $\left|\frac{\rho}{\rho^{\cdot}}\right|$ as a measure of the relative contributions of radical effects in the corresponding model series. Thus it was shown that the ratio $\left|\frac{\rho}{\rho^{\cdot}}\right|$ for the reaction series of monosubstituted toluenes used by Fisher and Meierhoefer[55] to determine polar effects amounts to 4.8, whereas an analogous model series of substituted toluenes containing a cyano group in the *meta*-position is described by a ratio of polar to resonance effect equal to 1 : 1.51; in addition, the accuracy to which each contribution has been determined does not provide the possibility of their correct separation.

It should be noted that many researchers[4,52,77,114,115] proposed their own scales of $\sigma^{\cdot}$ constants which they considered to be the most suitable for estimating the radical character of transition states. For instance, Jackson *et al.*[56] used the $\sigma^{\cdot}_{J}$ scale and demonstrated that in the transition states of the model homolytic reactions that underlay the Fisher–Meierhoefer radical constants $\sigma^{\cdot}_{FM}$ and the E_R and E_D parameters, the fraction of structures corresponding to the proper benzyl radicals is not more than 50%.

The authors of most of the approaches discussed above have attempted to formulate the requirements to an ideal model system to be used for kinetic determination of radical constants.

1. The substituents should interact directly with the radical centre.

2. The mechanism of the model reaction should be as clear as possible.

3. Side reactions should be minimised.

4. Model systems should be preferred in which substituents have a strong influence on the reaction rate and for which accessible and precise methods for the determination of relevant kinetic parameters exist.

5. The polar effects should be either absent or minimised, or be reliably separated from the effect of radical stabilisation.

6. The model compounds should be readily available and should contain diverse substituents of both electron-donating and electron-withdrawing natures.

7. The role of other external and internal factors, for example, the solvent and the steric effect, should be minimised.

8. One of the most important features required for a free-radical reaction to be used as a model to describe the radical effects of substituents is that the nature of the transition state should be as radical as possible.

According to the Hammond postulate,[116] the last-mentioned condition (this is very important to emphasise) implies a late transition state of the process, which corresponds to a more endothermic generation of free radicals. This, in turn, stipulates a higher selectivity of the reaction.[117] Therefore, the radical effects of substituents (in particular, the captodative effect† of radical stabilisation) are often considered in the context of selectivity of free-radical processes (see, for example, Refs 45, 118).

It should be noted that in none of the above-listed approaches, the transition state can be considered completely radical — in any case, one should suggest the presence of charge separation and polar interactions. Therefore, the topicality of the question of to what extent a particular scale of radical constants is free from the polar constituent is beyond doubt. Apparently, the polar constituent can hardly be ruled out completely.

2. Spectroscopic determination of the capacity of substituents for delocalisation of spin density in free radicals

Physicochemical methods such as EPR spectroscopy permit direct investigation of the properties of free radicals.

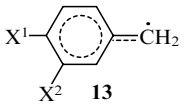
According to the McConnel equation

$$a_H = Q\rho^{\pi}_C,$$

the hyperfine splitting (HFS) constants a_H in the EPR spectra are directly proportional to ρ.[118]

For a number of compounds, the relative HFS constants have been found[119,120] to correlate with the σ and σ^- polar constants; it was concluded[119] that delocalisation of an electron pair is a more substantial stabilising factor than spin density delocalisation. A non-kinetic scale of the stability of alkyl radicals based on HFS constants of β-protons has been composed.[121]

The approach proposed by Arnold *et al.*[122–126] is best known of all; according to this approach, the HFS constants of α-protons are used as a measure of stabilisation energy, determined by delocalisation of spin density in substituted benzyl radicals **13** with respect to $PhC\dot{H}_2$.



13

This method has obvious advantages, which include the absence of side radical reactions and the relative ease of generation of the required free radicals.[45] In addition, the radical constants $\sigma^{\cdot}_{\alpha}$, defined by the equation

$$\sigma^{\cdot}_{\alpha} = 1 - \frac{a(H_X)}{a(H_0)}, \quad (10)$$

where $a(H_X)$ and $a(H_0)$ are the HFS constants of the α-protons in the substituted and unsubstituted radicals, respectively, can be considered to be free from the polar effects characteristic of radical-like transition states and do not correlate with the substituent effects in the corresponding diamagnetic initial compounds. The researchers[122] assumed that other factors which can potentially influence the HFS constants (hybridisation of the orbital bearing the unpaired electron, interaction with β-substituents, steric effects reflected in the geometry of benzyl radicals[118]) are insensitive to the substitution in the aromatic ring.

The $\sigma^{\cdot}_{\alpha}$ values thus obtained (Table 2) confirmed that the *meta*-substituents in the aromatic ring decrease delocalisation of the unpaired electron. The correlation established between the constants of *meta*-substituted benzyl radicals and the corresponding Hammett *meta*-constants (σ_m) made it possible to relate the destabilising effect of *meta*-substituents to their inductive electron-withdrawing effect.[45] However, it is not entirely clear why electronegative *meta*-substituents hamper delocalisation of spin density on the methylene carbon atom in the benzyl system.[124]

† Captodative effect is a joint influence of electron-donating and electron-withdrawing substituents on a radical reaction centre, resulting in a stabilisation greater than the sum of the two stabilising effects in the corresponding monosubstituted radicals.[45]

Table 2. Constants characterising the radical-stabilisation properties of substituents (from EPR data and bond energies).

Substituent	$\sigma^{\cdot}_{\alpha}(p)$ see [a]	$\sigma^{\cdot}_{\alpha}(m)$ see [a]	ΔD_p see [b]	ΔD_m see [b]	E_d see [c]	$\sigma^{\cdot}_{av}$ see [d]	RRS_X see [c]
H	0.000	0.000	0.00	0.00	104.4	0.00	0.0
Me	0.015	−0.001(0.002)	0.02	−0.09	100.3	0.23	2.3
OMe	0.034(0.018)	−0.001	−0.05	−0.15	93.3	0.35	4.5
NO_2	–	–	0.90	−0.06	–	0.76	9.4
CN	0.043(0.040)	−0.039(−0.026)	0.54	−0.14	92.9	0.63	8.6
F	−0.011	−0.018(−0.009)	−0.17	–	101.0	−0.03	−1.4
Cl	0.017(0.011)	−0.001(−0.007)	0.09	−0.08	99.2	0.18	2.4
Br	–	–	0.05	–	102.5	0.23	0.9
I	–	–	0.04	−0.09	103.4	–	0.2
OH	–	–	−0.05	−0.22	95.0	–	3.1
C(O)Me	0.066 (0.060)	–	–	–	–	0.58	10.2
$P(O)(OEt)_2$	–	–	–	–	–	–	–
$P(S)(OEt)_2$	–	–	–	–	–	–	–
Ph	–	–	–	–	87.9	0.59	11.2
SMe	0.063	–	–	–	–	0.55	10.7
SPh	0.058	–	–	–	–	–	10.7
CF_3	0.001(−0.009)	−0.014(−0.017)	0.11	−0.04	106.7	0.09	−0.3
OPh	0.018	−0.013(−0.002)	–	–	–	–	4.9
CO_2Et	–	–	–	–	–	–	–
CO_2Me	0.048(0.043)	−0.004	0.53	–	–	0.54	7.9
C(O)Ph	0.064(0.055)	–	–	–	–	0.65	9.3
Bu^t	0.036(0.008)	–	–	–	93.9	0.13	3.0
Et	0.012	–	–	–	99.7	–	1.5
Pr^i	0.009	–	–	–	–	–	–
SOMe	0.006(0.018)	–	–	–	–	–	4.1
SC(O)Me	0.029	–	–	–	–	–	6.7
S(O)OMe	0.016(0.005)	–	–	–	–	–	3.6
SO_2Ph	0.018	–	–	–	–	–	4.5
S(O)Ph	0.026	–	–	–	–	–	5.9
SO_3Me	0.003(0.013)	–	–	–	–	–	2.9
OC(O)Me	0.001(−0.005)	−0.014	–	–	–	–	0.9
OC(O)Ph	0.000	–	–	–	–	–	0.0
N=NPh	–	–	–	–	–	–	–
NH_2	–	–	0.30	−0.19	94.0	–	8.4
NMe_2	–	–	–	–	84.0	–	8.9
$SiMe_3$	–	–	–	–	–	–	3.5
$CH=CH_2$	–	–	–	–	86.7	–	12.8

Note. E_d is the energy of homolytic dissociation of the C−X bond in substituted methanes.
[a] From Refs 114, 125; [b] from Ref. 127; [c] from Ref. 45; [d] from Ref. 115.

Presumably,[124, 128] a decrease in the electron density by the inductive mechanism prevents the effective overlap of the interacting sites, *i.e.*, of the orbital carrying the unpaired electron with the π-system of the benzene ring, or, in other words, it decreases the energy of the π-system and thus weakens the interaction between the CH_2-group carbon and the aromatic ring.

The effects of the OC(O)Me, CF_3 and F groups located in the *para*-position were found to destabilise the radical centre, whereas other *para*-substituents, according to the data obtained from EPR, favour spin density delocalisation.

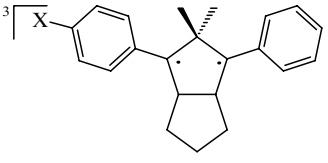
It has been suggested that a decrease in the spin density in the α-position of the benzyl radical would result in an increase in the π-resonance binding of the aromatic system with the methylene group and, correspondingly, in an increase in the barrier to rotation around the $C_{arom}-CH_2$ bond.[45, 124] The π-component of the stabilisation energy (E_s) of the π-radical was expressed *via* the rotation barriers of the CH_2 group in the $Z\dot{C}H_2$ radicals with or without spin density delocalisation

$$E_s = V_2(\dot{C}H_2) - V_2^*,$$

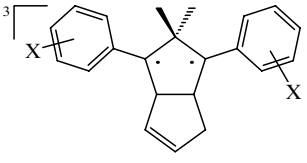
where the corresponding rotation barriers (V_2 and V_2^*) can be determined from EPR data.

Jackson [129, 130] has noted that the range of HFS constants considered by Arnold *et al.*[122–126] is rather narrow and some individual values were determined with substantial errors. Therefore, he developed a new approach that provided more accurate determination of the HFS constants $a(CH_2)$ in the EPR spectra of benzyl radicals.[116] The results [129, 130] are generally consistent with the $\sigma^{\cdot}_{\alpha}$ scale.

Yet another example of using quantitative parameters of EPR spectra is a study by Adam *et al.*,[127, 131–135] who made use of the electronic spin–spin splitting parameters *D*. The parameter *D* is a sensitive function of the averaged distance between the unpaired electrons in a biradical ($D \propto 1/r^3$) which is proportional to the product of local spin densities in the triplet biradicals **14** and **15**, chosen as the reference species to determine the capacity of the substituent X for spin density delocalisation.[130–132]



14



15

Proceeding from the assumption that specific electronic effects (captodative stabilisation, spin polarisation, *etc.*) are relatively insignificant in 1,3-biradicals,[136] Adam *et al.*[127, 132–134] proposed the scale of $\Delta D = D_H - D_X$ values (where H corresponds to the unsubstituted radical), which reflects delocalisation of the unpaired electron by the aryl group. Negative ΔD values, which should correspond to electron-donating groups, were found for all *meta*-substituents (including charged ones, *viz.*, NH_3^+, O^-) and for *para*-substituents such as F, OMe, OC(O)Me and OH. The *para*-substituents NO_2, CN, C(O)OMe, NH_2 and CF_3 exhibit the highest capacity for spin density delocalisation (see Table 1).

The additivity of ΔD values found for monosubstituted and symmetrically disubstituted triplet biradicals **14** and **15** served as the basis for the assumption that each of them can be represented as composed of two fixed fragments of the cumyl radical. Hence, the researchers suggested[127, 132] that the ΔD scale could also be used for adequate description of benzyl monoradicals. This suggestion is supported by the fact that the parameters D for triplet biradicals are correlated with the α-spin densities and the energies of resonance stabilisation of the corresponding cumyl radicals.[127, 132–134]

Comparison of the ΔD scale with known radical constants based on the properties of benzyl radicals revealed a relatively good correlation of this scale with the Fisher data (the correlation coefficient squared is $r^2 = 0.92$); however, the discrepancies with the $\sigma_J^{\cdot}$, $\sigma_C^{\cdot}$, and $\sigma_{JJ}^{\cdot}$ arrays are quite substantial ($r^2 = 0.33–0.60$). Subsequently, this approach has been extended to heteroaromatic π-systems such as pyridine and furan derivatives and some other.[135]

3. Thermodynamic approaches to the estimation of radical stabilisation. Bond energy as a measure of radical stabilisation

Study of the effects of substituents in free radicals is tightly connected with the problem of quantitative evaluation of the energies of dissociation of chemical bonds.

The energy of an R–R′ bond is known[136] to be determined by the enthalpy ΔH_1^0 of homolytic dissociation of this bond, giving rise to free radicals R$^{\cdot}$ and $\dot{R}'$

$$R-R' \longrightarrow \dot{R} + \dot{R}' .$$

In turn, the ΔH_1^0 value is determined by the standard enthalpies of formation of RR′, R$^{\cdot}$ and $\dot{R}'$

$$\Delta H_1^0 = \Delta H^0(\dot{R}) + \Delta H^0(\dot{R}') - \Delta H^0(RR') .$$

Thus, the relative energies of the homolytic dissociation of bonds can serve as a measure of radicals stabilisation. On the basis of the foregoing, Benson and O'Neal[137, 138] have proposed estimating the stabilisation energy for π-resonance delocalised radicals R(π-$\dot{C}H_2$) as the difference between the dissociation energies E_d of the corresponding derivatives

$$E_s[R(\pi\text{-}\dot{C}H_2)] = E_d[R(CH_2-H)] - E_d[R(\pi\text{-}CH_2-H)].$$

Subsequently, the C–H bond energies have been widely used to estimate the stabilisation energies for carbon-centred radicals. For example, the resonance stabilisation energy of the benzyl radical can be represented as the difference between the energy of the benzylic bond in toluene and the energy of the C–H bond in ethane.[45, 139, 140] The enthalpy of dissociation of the C–H bond in the methane molecule $E_d(CH_3-H) = 439$ kJ mol^{-1} is used most often as the reference value.[140–145]

In one of the first studies dealing with this topic, the enthalpy of the isodesmic reaction (*i.e.*, a reaction in which the number and character of bonds do not change on passing from the initial compounds to the products)[146]

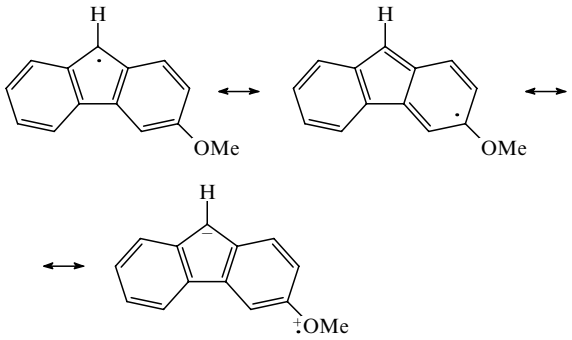
$$R^{\cdot} + CH_4 \longrightarrow RH + {}^{\cdot}CH_3$$

was identified as the stabilisation energy E_R of the R$^{\cdot}$ radicals[146]

$$E_R(R^{\cdot}) = \Delta H_2^0 = E_d(CH_3-H) - E_d(R-H).$$

Subsequently, stabilisation energies of radicals expressed in terms of E_d, *i.e.*, $E_s(R^{\cdot}) = E_d(CH_3-H) - E_d(R-H)$, have been widely used for various correlations.[138–145]

Bordwell *et al.*[147, 148] have proposed a scale of redox potentials I_{AO}, which is also actually based on the relative energies of dissociation of bonds in substituted fluorenes.



The potentials were determined using the thermodynamic cycle

HA	⟶	$H^+ + A^-$	(pK_a)
A^-	⟶	$A^{\cdot} + e^-$	(E^{ox})
$H^+ + e^-$	⟶	$H^{\cdot}$	(E^{red})
HA	⟶	$H^{\cdot} + A^{\cdot}$	(E_d),

in which the proton reduction potential E^{red} is a constant and the sum $pK_{HA} + E^{ox} = I_{AO}$ can be regarded as a measure of relative radical stability of the radical A$^{\cdot}$.

The oxidation potentials E^{ox} of substituted fluorenide ions were determined experimentally in DMSO solutions, and the pK values of the conjugate acids were established on the basis of their correlation with E^{ox}; this gave rise to a scale of I_{AO} values for a number of substituents at the 2-, 4- and 7-positions expressed in kJ mol^{-1} and reflecting the ability of these substituents to delocalise the unpaired electron in fluorenes.

The application of this approach to 9-substituted fluorenes and to 3- and 4-substituted phenylacetonitriles has made it possible to analyse a wide spectrum of radical-stabilisation and -destabilisation effects.[149, 150] Comparison of the I_{AO} values for 4-substituted arylacetonitriles with the $\sigma_{JJ}^{\cdot}$ constants within the framework of a two-parameter equation containing the σ^+-parameter showed that the contributions of the polar and radical constituents to I_{AO} are approximately equal.[58]

It has been proposed to use the E^{ox} oxidation potentials of 3- and 9-substituted fluorenes[150, 151] and of α-substituted acetone and acetophenone derivatives[152] in DMSO as the basis for determination of the stabilisation energies E_{RS} of the corresponding radicals

$$\Delta E_d = 1.37\Delta pK_{HA} + 23.1\Delta E^{ox}(A^-) = E_{RS}.$$

The resulting values point to a stabilising effect of substituents at the 3-position in substituted fluorenyl radicals, except for F and $PhSO_2$. Substitution into the 9-position both by donors and by acceptors results, as a rule, in system stabilisation. Most of 4-substituents (except for F and CF_3) also exhibit pronounced stabilising properties.[148] In general, it was concluded[150] that the majority of substituents play a dual role in the stabilisation of a free radical: they destabilise the radical due to the electron-acceptor influence and stabilise it due to delocalisation.

In some studies, the radical-stabilisation energy of substituent X was set identical to the covalent component of the dissociation energy of the XR–Z bond, where R is a permanent molecular fragment (for example, the aromatic ring), while R–Z is the 'indicator' bond.[140, 153–156] The notion 'indicator' bond was introduced back in Pauling's studies;[151] the stabilisation energy E_{RS} was defined *via* the relative dissociation energies of bonds in symmetrically substituted molecules

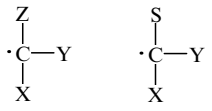
$$E_{RS} = 0.5\, E_d(XR-RX) - 0.5\, E_d(HR-RH).$$

A similar approach has been proposed by Leroy,[157, 158] who used the enthalpies of atomisation ΔH_a together with the standard bond energy E_{AB} to define the stabilisation energy E_s

$$E_s = \Delta H_a - \Sigma N_{AB} E_{AB},$$

where N_{AB} is the number of AB bonds. This procedure was applied successfully both to free radicals and to diamagnetic molecules.

Thermochemical and kinetic investigations of the rupture of the C—C bond have been employed to define the parameter E_{RS}, introduced to reflect the difference between the stabilities of the hydrocarbon radical **16a** and the corresponding substituted radical **16b**.[117, 156, 159–161]



16a **16b**

X, Y, Z are hydrogen atoms or alkyl substituents and S is a functional group.

A substantial drawback of the approaches in which the radical stabilisation is defined in terms of the relative bond energies and the reason why these approaches are severely criticised is the fact that the energy of homolytic dissociation of a bond is a relative value, *i.e.*, the difference between the energies of the molecule and the corresponding radicals; therefore, the substituent effect cannot be attributed to the properties of the free radical alone.[117, 143, 162, 163] It is well known that the dissociation energies of bonds depend on steric effects [116] and on polar effects;[164] the presence of numerous correlations between E_d(CH) and the 'ionic' constants of substituents σ^+ (see publications [23, 147, 165]) is common knowledge. In our opinion, this virtually rules out a legitimate separation of the polar and radical effects in this type of approach. Moreover, it was shown that in some cases, the effect of substituents can even prevail in the ground state; then the corresponding ΔE_d values reflect destabilisation of the molecule rather than stabilisation of the free radical.[163] It has been clearly demonstrated [143] using, among other reasons, vast literature data that relative bond energies cannot be related directly to the stability of radicals.

4. Calculation of the energies of stabilisation of radical centres

Apart from experimental methods, there also exist theoretical methods for the determination of group parameters of substituents reflecting their capacity for stabilisation of radical centres.

Modern quantum-chemical approximations permit direct calculation of quantitative characteristics of radicals such as the total energy, the standard enthalpy of formation, the energy of the orbital with the unpaired electron and the spin and charge density, which make it possible to judge the stabilising influence of substituents. Many quantitative parameters employed to determine the radical-stabilisation effects in terms of the experimental approaches described above such as the kinetic parameters of free-radical reactions and the overall thermodynamic characteristics, spin densities and rotation barriers in free radicals can be calculated quite reliably by quantum-chemical methods. Certainly, any general description of theoretical approaches requires separate consideration. Within the framework of this review, we shall dwell only on those of them that have served as the base for the introduction of sets (scales) of energetic parameters of substituents reflecting their radical-stabilisation influence and implying consistent utilisation of the LFE principle.

In studies by Pasto *et al.*,[166, 167] the change in the total energy of species participating in the free-radical transfer of a hydrogen atom has been identified with the stabilisation energy E_{RS} of the corresponding substituted methyl radical. The E_{RS} values were calculated for a large number of substituents. The captodative effect of radical stabilisation and the influence of the substituents attached to the reaction centre containing an unpaired electron were analysed from the additivity standpoint.[166] The comparison of the calculated E_{RS} values with the known scales demonstrated a relatively good quantitative agreement with the I_{AO} parameters for 3- and 9-substituted fluorenes and 4-substituted phenylacetonitriles,[148] with the relative constant of the thermal rearrangement of 3-aryl-2,2-dimethylmethylenecyclopropanes [57, 82, 83] and α-spin density in 4-substituted benzyl radicals.[114] Within the framework of this approach, it was found that the radical-stabilisation effect markedly increases on passing from F- to O- and N-containing substituents. In the series Cl, S, P, the capability for spin density delocalisation increases due to the decrease in the energy gap between the vacant MO of the methyl radical and the MO occupied by the unpaired electron. Study of the effects of substitution with charged ($^+NR_3$, $^+SR_2$, $^+PR_3$) or electronegative non-charged (CF_3, SOR, SO_2R) groups showed that they destabilised the radical. In addition, it was found that the energies of stabilisation of the radical centre calculated in terms of the approach proposed are exceptionally sensitive to the conformation of the free radical and the corresponding diamagnetic molecule.

Isodesmic reactions (see Section II.3) proved convenient for the calculation of $E_{RS}(R^{\cdot})$.[44, 144, 168–173] The enthalpy of hydrogen atom detachment in these reactions is a measure of the energy of stabilisation of the radical centre; the use of this value decreases the errors related to the basis set chosen and to electron correlation effects.[174]

The stabilisation energies of the radical centre E_{RS} correlated with the barriers to rotation around the C—C bond in benzyl radicals were calculated by quantum-chemical methods, as well as the difference between the energies of the conformers corresponding to angles of rotation around the σ-bond equal to 90° and 0°.[175–177]

$$E_{RS} = \Delta H_f(90) - \Delta H_f(0).$$

The E_{RS} values thus obtained are well correlated with the parameters D of the biradicals **14** and **15** determined experimentally by EPR.[127]

5. Critical analysis of the existing approaches

The attempts at systematisation of the existing radical scales of substituents made previously can be classified, in our opinion, into two main types, namely, the choice of the $\sigma^{\cdot}$-scale describing most accurately the standard homolytic reaction series and the development of a quantitative approach integrating the accumulated arrays of 'radical' constants and combining them into some universal scale.

We have already mentioned that the authors of many of the studies presented in the previous Sections proposed their own standard series; the corresponding arrays of the group parameters were regarded as most suitable for developing a scale that could be used as the reference in analogous approaches. However, the search for this optimal scale did not reveal obvious advantages of any of the known sets of radical parameters; therefore, in some cases, it was concluded [9] that development of universal radical constants $\sigma^{\cdot}$ is impossible in principle. The attempts to find multiparameter correlations with the use of various combinations of polar and radical scales did not produce a satisfactory general result either. Moreover, the methodology of using the extended Hammett equation for the description of radical-stabilisation effects has been criticised.[49]

In view of the difficulty of using group radical constants to describe homolytic processes, Hansch and Leo [178] proposed that the polar parameters σ should be used for this purpose whenever possible. Exner [179] also suggested that the σ_p^+ and $\sigma_{m,p}$ constants suffice for interpretation of the free-radical reactivity. In another study,[180] radical-stabilisation effects of substituents are described in terms of the quadratic function σ^2; this, in principle, contradicts the LFE formalism.

Several prominent researchers attempted, in a joint review,[45] to devise a universal scale of relative radical stabilisation (RRS), based on averaging of the above-mentioned scales of the Creary ($\sigma^{\cdot}_{C}$),[57,80–84] Jackson ($\sigma^{\cdot}_{J}$)[51,52,56,76–79] and Arnold ($\sigma^{\cdot}_{\alpha}$) constants,[114,122–125] the kinetic parameters of radical fragmentation of bis-azo derivatives[96–100] and a number of other analogous characteristics of free-radical reactions.[45,180–184] It was suggested that statistical averaging would eliminate the errors inherent in each of basic experimental approaches. In addition, the average group RRS parameters are expected to reflect the degree of additivity of the group influences upon multiple substitution at the carbon radical centre and to describe the effect of captodative radical stabilisation.

Positive averaged RRS_X values (see Table 2), which imply radical-stabilisation properties, were found for a large number of diverse substituents. The only exceptions were F and CF_3, for which the RRS_X(F) values were -1.4 and -0.3, respectively.

By means of the scale of averaged RRS_X, the researchers[45] were able to identify a number of interesting correlations which point, in particular, to underestimation of the radical-stabilisation properties of electron-withdrawing substituents and overestimation of the role of electron donors in terms of some $\sigma^{\cdot}$-approaches.

The averaged radical $\sigma^{\cdot}_{av}$ scale was based[115] on two sets of EPR characteristics of benzyl radicals taken from the literature[115,124] and on three 'kinetic' arrays, namely, scales of the $\sigma^{\cdot}_{C}$ (see Refs 57, 80–84) and $\sigma^{\cdot}_{J}$ (see Refs 50–52, 56, 76–79) constants and kinetic data taken from the literature.[101] The $\sigma^{\cdot}_{av}$ values (see Table 1) confirmed the radical-stabilisation properties of the vast majority of *para*-substituents including CF_3. Only the averaged constant for *p*-F was found to be negative ($\sigma^{\cdot}_{av} = -0.02$). This deviation was explained by assuming that, under the action of the electronegative F atom, hybridisation of the carbon atom at the 4-position changes somewhat towards sp^3; this disturbs the aromaticity of the benzene ring and, hence, destabilises the radical centre.

Each of the definitions of the radical $\sigma^{\cdot}$ constants characterised in this Section suffers from its own specific disadvantages. They were noted above whenever appropriate. In addition, the methods of description of the radical effects of substituent can be subjected to a common criticism. It is expedient to arrange critical remarks in accordance with the above classification.

1. Kinetic methods. It is known that the classical σ-constants of electron-withdrawing substituents, which stabilise an electron-enriched reaction centre, are positive, whereas electron-donating groups, which stabilise electron-deficient systems, have negative polar constants. In turn, the sign of the parameter ρ of the correlation equation reflects the character (either electrophilic or nucleophilic) of the reaction, while the magnitude of ρ shows the degree of charge separation in the transition state. It is commonly known that the polar constants of substituents correlate equally adequately with the properties of the transition state and the ground state (numerous polar scales are based on the physicochemical, for example spectroscopic, properties of neutral molecules). Thus, successful description of energy characteristics of heterolytic processes in terms of group constants is normally explained by assuming either that the substituent effects in the transition and ground states are correlated or that the latter can be neglected. The kinetic methods of determination of substituent effects in homolytic processes also deal with the difference between the energy of the ground and radical-like transition states. However, a significant specific feature of free-radical reactions is that the natures of the initial species (or products) and the transition state in any homolytic process are fundamentally different because of the presence of an unpaired electron; the effects of substituents on the energies of the ground and transition states differ not merely quantitatively, as in the case of heterolytic processes, but also qualitatively. Furthermore, the numerous examples cited in the preceding Sections point to the importance of substituent effects in the ground state of homolytic processes, which precludes the possibility of neglecting them. In addition, even if the polar interactions in the ground state are assumed to be proportional to those in the radical-like state, their role in delocalisation of the proper unpaired electron still remains obscure.

Strictly speaking, the magnitudes of radical $\sigma^{\cdot}$ parameters established by kinetic methods often reflect the differences between the influence of substituents on the initial and transition states of a particular reaction but not the effectiveness of delocalisation of the unpaired electron by one or another substituent. In this connection, the numerous examples of successful use of polar constants alone for the description of free-radical processes seem quite obvious and the lack of correlation between radical scales is quite logical. Thus, reasonable separation of the effects related to charge stabilisation and to delocalisation of the unpaired electron within the framework of kinetic approaches appears unlikely, if achievable at all.

It is also worthy of note that the role of other factors (steric effects and, especially, solvent effects) has been interpreted fairly arbitrarily in most of the approaches considered. As a rule, the authors assumed that the homolytic mechanism of the standard reaction allows the solvent effects to be completely neglected. However, as has already been noted, in reality, none of the kinetic approaches allows complete elimination of the influence of polar interactions (which can depend substantially on the properties of the medium); this casts doubt on the proper methodology of determination of many $\sigma^{\cdot}$-scales.

2. Spectroscopic methods. Methods based on the use of EPR for determination of the spin density distribution are free from the drawbacks associated with the substituent effects in the corresponding molecules. Meanwhile, the question of whether spin density delocalisation follows a linear correlation with the stabilisation energy of a free radical remains relevant. In addition, it is unclear to what degree the spin density distribution is governed by the delocalisation contribution and to what degree, by the spin-polarisation contribution.[45] And, finally, what is the role of polar effects (for example, resonance effects) in the spin density distribution? Is it proper to consider them insignificant and related exclusively to charge stabilisation?

In our opinion, the following circumstance is also rather important. Let us assume that the spectral $\sigma^{\cdot}$-constants do actually reflect the capacity of substituents for delocalisation of the unpaired electron. Then it is clear that valid considerations about the mechanisms of delocalisation of an unpaired electron by substituents can be constructed on their basis and the $\sigma^{\cdot}$ values can be used to verify the adequacy of similar approaches to the solution of problems for which the correlation analysis methods are meant. However, the scope of applicability of these spectral radical scales still remains vague, while their predictive capacity and practical application hardly possess considerable advantages. In any case, when describing real homolytic reaction series, the presence of polar interactions (which are always quite probable, as we have repeatedly emphasised above) implies the use of a two-parameter correlation equation containing both radical and polar constants. One or another polar scale can be preferred and the relationship between the polar and radical components of the stabilisation effect can be identified only on the basis of a statistical selection procedure. From a practical point of view, this brackets the $\sigma^{\cdot}$ constants obtained by spectroscopic methods with those determined by kinetic methods.

3. Thermodynamic methods. The approaches based on the use of thermodynamic methods are criticised especially vigorously. As has been mentioned above, determination of radical-stabilisation effects in terms of thermodynamic parameters (bond energies) corresponding to diamagnetic substrates does not permit one to rule out the substituent effects related to the molecules or to distinguish the proper radical stabilisation from polar or steric factors. Strictly speaking, these approaches are rather suitable for discussing the relative effects of substituents on the energies of covalent bonds; this, in itself, is a complex problem not ultimately solved. It is also noteworthy that, within the framework of

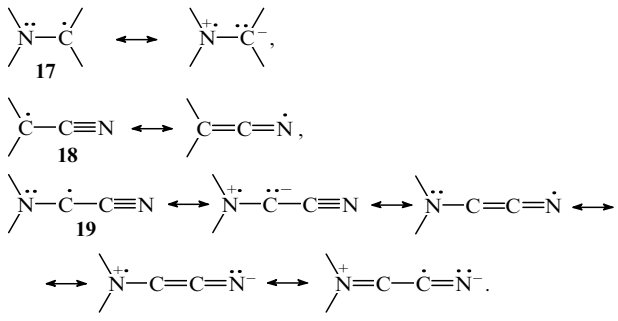
thermodynamic approaches, the radical stabilisation effect is largely replaced by the notion of radical stability. Strictly speaking, this is not the same; below we shall consider this point in more detail.

To conclude this section, it can be stated that none of the existing methods of $\sigma\rho$-description of substituent effects in free-radical processes is free from serious drawbacks and, as a rule, each method operates within a narrow reaction series. The lack of correspondence between radical scales and the different in kind interpretations of the radical-stabilisation properties of the same substituents in terms of different approaches make difficult the understanding of the physical meaning of radical constants and preclude the possibility of their joint application.

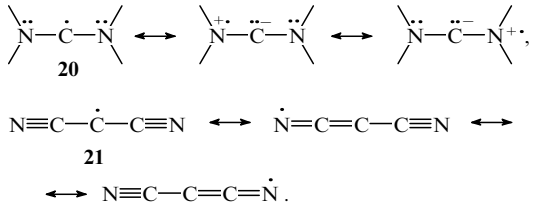
It cannot be ruled out that the correlation analysis formalism cannot, in principle, be applied in full measure to the description of homolytic processes because the additivity of group interactions is there violated. An especially clear example is the captodative stabilisation effect, or push – pull effect, repeatedly mentioned above.

4. Captodative effect. The existence of an extra-stabilisation effect peculiar to bifunctional radicals was first assumed by Dewar.[185] A quantitative proof of the unusual stability of these radicals was later presented in studies by Balaban *et al.*,[186, 187] who used the term 'push – pull resonance.' Later, Katritzky *et al.*[188 – 190] arrived at the conclusion that radical centres bearing simultaneously an electron-donating and an electron-withdrawing group are subject to an extra-stabilisation effect, which was called merostabilisation (later, captodative effect).[45,191 – 194]

A simple substantiation of the captodative stabilisation can be derived from the numbers of contributing structures [in the example presented below, there are two structures for the amino- (**17**) or the cyano-derivative (**18**)] corresponding to monosubstituted radicals and to a disubstituted radical containing both electron-donating and electron-withdrawing groups [five contributing structures are presented for the amino-cyano-substituted radicals **19**].



For disubstituted radicals containing either only amino- (**20**) or only cyano groups (**21**), three contributing structures can be proposed



Thus, stabilisation of these species due to delocalisation would be somewhat weaker than is expected based on the sum of the substituent effects in the monosubstituted analogues.

The over-additive stabilisation effect in radical species containing both electron-donating and electron-withdrawing groups has been repeatedly confirmed experimentally. The enhanced reactivity of captodative alkenes has been noted in radical [193 – 199] and [2 + 2]-cycloaddition [45, 199 – 202] reactions. The captodative acceleration was considered to be the reason explaining the results obtained in studies of cyclisation of 6-substituted hex-5-en-1-yl radical,[203] homosolvolysis of some alkyl bromides on treatment with di-*tert*-butylnitroxide,[204] thermal rearrangement of substituted 2-arylmethylenecyclopropanes,[205] isomerisation of diastereomeric substituted cyclopropanes [206, 207] and thermal homolysis of the C – C bond in hexa-1,5-dienes [207] and dibenzyls.[208, 209]

EPR data for substituted benzyl radicals point to enhanced stabilisation of those radicals that contain both electron-donating and electron-withdrawing substituents, whereas two identical substituents decrease radical stabilisation.[114] Analysis of the barriers to internal rotation and the energy barriers to *E*,*Z*-isomerisation of substituted allylic radicals determined from EPR data also attests in favour of captodative interactions.[210] Study of the barriers to rotation around the C – N bond in substituted aminoalkyl radicals has led to similar conclusions.[211] In several publications,[161, 212, 213] the captodative effect was substantiated from the standpoint of orbital views. Calculations of the stabilisation effects in free radicals also predict an enhanced stabilisation of captodatively substituted derivatives.[45, 163, 214, 215]

However, a number of experimental and theoretical studies have not elucidated any significant distinctive features of captodatively substituted radicals and demonstrated strictly additive influence of the corresponding substituents at a radical reaction centre.[216 – 219] Moreover, some researchers cast doubt on the existence of an additional captodative stabilisation. Within the context of the present consideration, we would only like to mention that, under the assumption of the existence of captodative stabilisation of free radicals, the use of additive correlation equations based on LFE and polylinearity principles to describe homolytic processes should be subject to certain, perhaps quite substantial, constraints.

Thus, analysis of the published data available to date provides grounds for the following conclusions.

1. The classical polar constants σ are not fully applicable to the description of free-radical processes and do not reflect the radical-stabilisation effects of substituents. In all probability, one can speak about a disproportion of substituent effects in heterolytic and homolytic processes. Although quite a few examples of successful use of polar constants in free-radical chemistry have been reported, the existing scales of specific radical constants $\sigma^{\cdot}$ are not general. The lack of correspondence between the scales and vagueness of their physical meaning might be due to the constrains inherent in the use of the LFE principles and correlation analysis in free-radical chemistry and violation of the additvity of the group influence in paramagnetic systems rather than to the drawbacks of the methods of their determination.

2. It is obvious that an approach, new in principle, to the description of substituent effects in free-radical systems needs to be developed. It is important that this approach should possess predictive capacity and provide a quantitative estimate of the character of interaction of substituents with the radical reaction centre. However, it is quite probable that the physical nature of this interaction would not be clarified completely but it would be possible to obtain a satisfactory quantitative description of the structure – reactivity relationship as applied to the chemistry of free radicals.

III. The use of r^{-2} analysis in free-radical chemistry

1. Modelling of inductive and steric effects

Previously, we have developed quantitative procedures for determination of the steric and inductive effects of substituents in terms of discrete atomic contributions. Detailed description and theoretical substantiation of the models proposed, aspects of their practical use and the inductive electronegativity concept based on them have been presented in our previous reviews.[2 – 6] In the context of this review, we considered it pertinent to mention the main theses of these approaches.

Steric interactions were determined in terms of the model of frontal steric effect in which the steric effect of a substituent is represented as a result of mechanical shielding of the reaction centre by the surrounding atoms

$$R'_S = \sum_{i=1}^{n} \frac{R_i^2}{4r_i^2}, \tag{11}$$

where R'_S is the steric constant, n is the number of atoms in the substituent, R_i is the radius of an ith atom and r_i is the distance from the ith atom to the reaction centre.

It should be emphasised that in terms of this approach, the steric effect of any substituent at any reaction centre can be predicted with high accuracy on the basis of only fundamental parameters (the size and the distance to the reaction centre) of the atoms forming the substituent. The R'_S parameters calculated for a broad range of the most frequently encountered groups follow a good correlation with the Taft steric constants ($N = 35$, $R = 0.9854$, $S = 0.141$).

In the model of inductive effect, the inductive constant σ^* of an n-atomic substituent was represented at the atomic additivity level

$$\sigma^* = \sum_{i=1}^{n} \frac{\sigma_{A(i)}}{r_i^2}, \tag{12}$$

where σ_A is an empirical constant introduced in the model of inductive effect and reflecting the ability of an atom to exhibit the inductive effect, which depends on the nature and valence state of the atom. The σ_A values have been established for a wide range of elements; the inductive constants calculated theoretically using these values (altogether 426 substituents) have formed a high-quality correlation with the corresponding experimental data ($N = 426$, $R = 0.9910$, $S = 0.190$).

The practical use of this additive approach in the description of reactivity and investigation of the mechanisms of reactions involving organic and heteroorganic compounds proved fairly successful. This has also contributed to the solution of a number of important theoretical problems related to inductive interactions such as the inductive effect of alkyl substituents, the presence or absence of linearity in the inductive effects of substituents on carbon and heteroatom reaction centres and some others. The models developed make it possible to describe quantitatively only the inductive and steric effects; no approach based on the modelling principle for estimation of resonance interactions has been devised yet. Nevertheless, as shown in our study,[4] the additive model of inductive effect describes rather adequately the electronic interactions in various conjugated systems and only some of them, subjected to the influence of direct polar conjugation, can provide exceptions.

2. Combinational approach. r^{-2}-Analysis. Ionisation energies of amines

The new topological approach developed on the basis of the above models, which allows the substituent effect to be expressed in terms of discrete atomic contributions, was first reported in our publication and called r^{-2}-analysis.[220]

Since both the steric and inductive constants were expressed in Eqns (11) and (12) as functions of $1/r^{-2}$, the two-parameter Taft equation

$$Y = \rho \sum_i \sigma^* + \delta \sum_i E_s \tag{13}$$

can be represented in terms of discrete atomic contributions

$$Y - Y^0 = \sum_{i \neq rc}^{N-1} \frac{e_i}{r_{rc-i}^2}, \tag{14}$$

where N is the number of atoms in the molecule, rc is the atom chosen as the reaction centre, r_{rc-i} is the distance between atom i and the reaction centre. The dependent parameter Y can be represented by any physical value which is used in terms of a general correlation equation (13) (the logarithm of the rate or equilibrium constant, the reaction or activation energy, *etc.*), Y^0 is the same parameter for a compound chosen as the standard in this reaction series, and e is a parameter reflecting the capacity of an atom of a definite type for exhibiting intramolecular effects determining the Y values.

The approximation we used permits one, first of all, to verify whether it is possible, in principle, to introduce the operational atomic constants e_i corresponding to atoms of different types and depending on the nature and the valence state. The next step is to determine their physical meaning. The formalism of this approach implies that each atom encountered in all the molecules of the reaction series can, in principle, be regarded as a hypothetical reaction centre. In this case, for each molecule contained in the reaction series, the other $N-1$ atoms are treated as a single sub-substituent.

After the reaction centre for a given series has been chosen, the matrix of sums

$$\sum_k \frac{1}{r_{rc-m_k}^2},$$

corresponding to the types of atoms present should be composed. A table should be made up, containing N vertical matrix elements (rows), where N is the number of molecules in the reaction series, and M horizontal elements (columns),where M is determined by the types of atoms represented in the molecules of the series. The k value in the matrix of sums corresponds to the number of atoms of type m in molecule n, and $r_{rc-m_k}^2$ are the distances between type m atoms and the reaction centre rc in molecule n. If no type m atoms are present in molecule n, the corresponding matrix element is taken to be zero. As an example, Table 3 gives the r^{-2}-matrix for the reaction series including the $MeH_2C^{\cdot}$, $ClH_2C^{\cdot}$, and $Me(NH_2)HC^{\cdot}$ radicals in which the carbon bearing the unpaired electron is chosen as the reaction centre. In real calculations, the number of horizontal elements should exceed the number of vertical elements; then the columns of this matrix can be regarded as sets of independent arguments and the $Y - Y^0$ array can be regarded as an array of dependent values of multiparameter linear regression (14).

Table 3. r^{-2}-Matrix for the reaction series containing the $MeH_2C^{\cdot}$, $ClH_2C^{\cdot}$ and $Me(NH_2)HC^{\cdot}$ radicals.

Radical	Type of atom			
	H	C(sp^3)	Cl	N(sp^3)
$MeH_2\dot{C}$	$\frac{2}{1.09^2} + \frac{3}{2.16^2}$	$\frac{1}{1.54^2}$	0	0
$ClH_2\dot{C}$	$\frac{2}{1.09^2}$	0	$\frac{1}{1.76^2}$	0
$Me(NH_2)H\dot{C}$	$\frac{1}{1.09^2} + \frac{3}{2.16^2} + \frac{2}{2.04^2}$	$\frac{1}{1.54^2}$	0	$\frac{1}{1.46^2}$

Thus, if the corresponding multiparameter correlation can be established with a satisfactory accuracy, its linear coefficients are the operational atomic constants e_i corresponding to particular types of atoms. It is clear that this scheme should be effective in the description of those reaction series that can be analysed quantitatively using inductive and steric group constants.

The method developed for the description of substituent effects has several obvious advantages over classical correlation analysis. First, it is free from the restrictions associated with the choice of an appropriate scale of substituents because it deals directly with interatomic distances and is conformationally sensitive. Second, the use of a simple mathematical apparatus allows one to analyse quickly and effectively indefinitely large sets of

parameters. Third, within the framework of this model, it becomes possible to consider all the potential reaction centres of the series, which can provide additional information on the mechanism of the process under study. This is important in those cases where interpretation of the mechanism does not appear unambiguous and variation of the reaction centre could permit decision in favour of one of the most probable mechanisms.

We implemented the algorithm outlined above as a product called RMATRIX, which was developed on the basis of the MATLAB program.[221] The RMATRIX program allows importing of intramolecular distances from HyperChem or from similar files containing data on the spatial structure of the molecules of a reaction series; then it composes the r^{-2}-matrix corresponding to the reaction centre chosen for each molecular series, and, finally, it establishes statistically the operational atomic increments e for the series.

3. The physical meaning of the operational atomic parameters

A drawback of r^{-2}-analysis is that it does not allow direct consideration of resonance interactions because they cannot be described certainly by any distance function. However, a more substantial problem is that the physical meaning of the operational atomic parameters e_i, defined by Eqn (14), remains vague and does not provide the possibility of resolving the substituent effects into the inductive and steric components. The analysis of the e_i values presented below is pertinent in this connection. The correlations established previously in terms of the steric and inductive models can serve as the basis for this consideration.

Thus it has been found[4] that the σ_A constants for a broad range of elements are correlated with the difference between Pauling's electronegativities $\Delta\chi_{i-rc}$ of a given element A and the atomic reaction centre (rc) (this difference reflects the ability of atom A to displace electron density) and with the squared covalent radius of the A atom (which reflects its capacity for charge delocalisation)[4, 5, 222]

$$\sigma_A = 7.84\Delta\chi_{i-rc}R_i^2 .$$

The back calculation of the χ values using this relation makes it possible to introduce a new scale of 'inductive' electronegativities, which is purely empirical because it is based on the inductive constants describing a huge array of reaction series.[4, 5] This scale is, by definition, in good agreement with Pauling's electronegativities, except that for carbon. According to the 'inductive' scale, the electronegativity of carbon is 2.1. This value appears to be more plausible than $\chi^P = 2.55$ proposed in the Pauling scale.[2, 223, 224] The latter value implies that carbon should be more electronegative than, say, phosphorus ($\chi^P = 2.2$) or iodine ($\chi^P = 2.4$), which is not the case in reality. The low polarity of the C—H bond also indicates that the Pauling χ^P value for carbon is overestimated. Subsequently, a scale of group inductive electronegativities and the concept of inductive chemical hardness, which interpret a number of widely used reactivity indices using simple geometrical characteristics of bonded atoms, have been developed in terms of this approach.[2] These concepts were considered in detail in our review [2] and in a number of publications.[223–231]

On the basis of established correlations, the Taft inductive constant can be expressed in terms of fundamental characteristics of the atoms of substituents and the reaction centre, namely, electronegativities, radii and interatomic distances

$$\sigma^* = 7.84\sum_i \frac{\Delta\chi R_i^2}{r_i^2} . \qquad (15)$$

By superposition of Eqns (11)–(14), the atomic parameters e_i can be represented as the sum of inductive and steric constituents

$$e_i = a\Delta\chi_{i-rc}R_i^2 + bR_i^2 . \qquad (16)$$

Evidently, if a satisfactory correlation of type (16) has been established, it becomes possible not only to calculate the unknown e_i values on its basis but also to express the dependent parameters Y in terms of inductive and steric Taft constants as an ordinary two-parameter equation (13). If the 'inductive' electronegativity of the reaction centre atom is unknown, the e value can be found using the two-parameter correlation

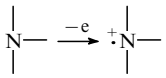
$$e_i = a'\chi_i R_i^2 + b'R_i^2 , \qquad (17)$$

where the coefficient b' includes the χ_{rc} value.

It should be emphasised that correct separation of the inductive and steric effects requires that the nature (electronegativity) of the reaction centre be known exactly and, in any case, it implies certain assumptions. Nevertheless, the corresponding atomic operational constants e_i still can be employed to predict the unknown Y values for related molecular systems consisting of atoms with known e_i even in those cases where correlations (15) and (16) cannot be established.

Except for the inapplicability for the description of the resonance effect, the method under discussion does not have any serious limitations and can be used successfully even in those cases where the standard empirical scales are ineffective. The quantitative description of the vertical and adiabatic ionisation potentials of amines performed in our study exemplifies the practical application of the r^{-2}-scheme.[221]

Previously, the dependence of the ionisation potentials of a limited range of amines on their structure has been interpreted with utilisation of a large number of independent parameters both those reflecting particular inductive, resonance and polarisation effects and those chosen rather arbitrarily.[232]



We attempted to consider the ionisation potentials of amines in terms of the unified approach developed and composed the corresponding r^{-2}-matrix in which the nitrogen atom was chosen as the reaction centre. The adiabatic and vertical ionisation potentials (I^{ad}, I^{vert}) of amines in the gas phase, taken from a publication,[233] were analysed in terms of the parameters of the basic equation (14). As a result, reliable multiparameter correlations were established for the sets of adiabatic and vertical potentials

$$I^{vert}_{R_3N} = \sum_i^{N-1} \frac{i_i^{vert}}{r_i^2} + const_1 \ (R = 0.954, S = 0.331, N = 287), \qquad (18)$$

$$I^{ad}_{R_3N} = \sum_{i=1}^{N-1} \frac{i_i^{ad}}{r_i^2} + const_2 \ (R = 0.960, S = 0.341, N = 231), \qquad (19)$$

where N is the number of atoms in the amine molecule and i_i^{vert} and i_i^{ad} are the operational atomic parameters reflecting the capacity of the atom of a definite type for participation in intramolecular interactions, which determine the I^{vert} and I^{ad} values, respectively.

The following fact attracts attention: although we analysed arrays of the absolute values of I^{ad} and I^{vert} not referred to any standard, the free terms of multiparameter correlations (18) and (19) determined statistically actually reproduced the corresponding ionisation potentials of the ammonia molecule.

The values of the $i^{ad/vert}$ parameters were then analysed using Eqn (16); the following correlations were identified:

$$i^{ad} = 4.55(\chi - 2.79)R^2, \qquad (20)$$

$$i^{vert} = 4.38(\chi - 2.98)R^2. \qquad (21)$$

Thus, the correlations found allow the calculation of the unknown parameters $i^{ad/vert}$ and, hence, the previously unknown ionisation potentials of amines from atom electronegativities and covalent radii. Moreover, if the role of steric effect during electron transfer is assumed to be insignificant (which appears quite reasonable), values of 2.79±0.7 and 2.98±0.7 found using these

relations are in a fairly good agreement with the inductive electronegativity of nitrogen (2.56, see Ref. 223).

4. Ionisation energies of free radicals

The possibility of quantitative determination of the energies of oxidation of amines to the corresponding radical cations using the approach we developed points to its adequacy and applicability to free-radical processes. As noted above, the examples of quantitative interpretation of the reactivity of free radicals currently available are limited, as a rule, to aromatic systems.

We attempted to apply the r^{-2}-analysis to electron transfer, which is one of the least studied homolytic reactions from the standpoint of 'radical' effects of substituents. We did not restrict ourselves to narrow series of aromatic compounds but considered single-electron processes involving diverse C-, N-, S- and O-centred radicals both belonging to aromatic and aliphatic series.[233, 234] The single-electron ionisation potentials of free radicals in the gas phase were taken from a database [235] and analysed in terms of our approach.

a. Carbon-centred radicals

In accordance with the approach developed, the ionisation potentials (I) and electron affinities (A_e) of carbon-centred radicals were analysed using the equations

$$I_{R^\cdot} - I_{Me^\cdot} = \sum_{i \subset R} \frac{e_i^+}{r_i^2} \text{ and} \tag{22}$$

$$A_e(R^\cdot) - A_e(Me^\cdot) = \sum_{i \subset R} \frac{e_i^-}{r_i^2}, \tag{23}$$

in which the I and A_e values for the methyl radical are included as reference values provided that the carbon atom bearing the unpaired electron is taken to be the reaction centre.

The multiparameter correlations (22) and (23) were established with high accuracy. The operational parameters e^+ and e^- found from relations (22) and (23) are presented in Tables 4 and 5 together with the corresponding values for the inductive electronegativities and the covalent radii of atoms. By comparing them in terms of a type (17) relation, we expressed the e^+ parameters in the form

$$e_i^+ = (1.09 \pm 0.33)\chi_i R_i^2 - (5.49 \pm 0.97) R_i^2 \tag{24}$$

(the O, N and S atoms were not included in the correlation) or

$$e_i^+ = 1.09(\chi_i - 5.04) R_i^2 .$$

Thus, the ionisation potentials of C-centred radicals in the gas phase can be expressed in terms of fundamental parameters of atoms

$$I = I_{Me^\cdot} + 1.09 \sum_{i=1}^{N} \frac{(\chi_i - 5.04) R_i^2}{r_i^2} . \tag{25}$$

Relations (24) and (25) demonstrate that the vast majority of atoms [except highly electronegative ones such as *sp*-hybridised N atom ($\chi = 6.76$)] introduced in the environment of the C$^\cdot$ reaction centre decrease the corresponding ionisation energy relative to that of the methyl radical. The deviation of the atomic parameters e^+ for O, N and S atoms from the general pattern of dependence is apparently due to the resonance effect, which cannot be described from the standpoint of the given approach, as has been repeatedly mentioned above. To elucidate the reasons for this deviation, a special detailed analysis is required; we plan to perform it subsequently. In addition, analysis of the predicted ionisation potentials demonstrates a substantial deviation of the I_{pred} value for the methyl radical, which is a typical problem for this type of approach. Since the methyl radical was chosen as the reference species ($\Delta I = 0$), its e^+ parameter should, by definition, be equal

Table 4. Operational atomic parameters e^+_{emp} found from experimental ionisation potentials and the corresponding e^+_{calc} values calculated using correlation (17).

Radical centre	Atom	χ_i	R^2	e^+_{emp}	e^+_{calc}	$e^+_{emp} - e^+_{calc}$
C$^\cdot$	C	2.10	0.593	−1.86±0.11	−1.90	0.04
	H	2.10	0.090	−0.25±0.04	−0.29	0.04
	C(arom.)	2.45	0.449	−1.45±0.14	−1.27	−0.18
	C(sp^2)	2.25	0.449	−1.78±0.14	−1.37	−0.41
	C(*sp*)	2.65	0.390	−0.80±0.39	−0.55	−0.25
	Cl	3.09	0.980	−1.91±0.19	−2.09	0.18
	Br	2.97	1.299	−2.73±0.23	−2.94	0.21
	F	3.93	0.409	−0.78±0.10	−0.50	−0.28
	S	2.67	1.082	−6.61±0.58	−2.78	−3.83
	O	3.05	0.436	−3.77±0.27	−0.95	−2.82
	N	2.56	0.490	−6.15±0.26	−1.33	−4.82
	N(*sp*)	6.76	0.3025	5.888	0.562	5.326
N$^\cdot$	C	2.10	0.593	−6.202±1.361	−5.70	−0.502
	H	2.10	0.090	−0.217±0.485	−0.87	0.653
	N	2.56	0.490	−5.996±2.652	−4.46	−1.536
	C(arom.)	2.45	0.449	−1.934±1.088	−4.14	2.206
O$^\cdot$	C	2.10	0.593	−5.407±0.534	−6.22	0.813
	H	2.10	0.090	0.022±0.327	−0.94	0.962
	O	3.05	0.436	−3.663±0.799	−2.93	−0.733
	Cl	3.09	0.980	−6.307±1.052	−6.45	0.143
	F	3.93	0.410	−0.498±0.748	−1.34	0.842
	Br	2.97	1.300	−8.942±1.244	−9.17	0.228
	I	2.80	1.769	−14.25±1.51	−13.66	−0.59
	C(arom.)	2.45	0.449	−4.071±0.348	−4.09	0.019
S$^\cdot$	C	2.10	0.593	−3.370±1.831	−4.57	1.2
	H	2.10	0.090	0.003±1.089	−0.69	0.693
	S	2.67	1.082	−8.680±2.598	−7.25	−1.43
	F	3.93	0.410	−0.814±1.848	−1.88	1.066
	C(arom.)	2.45	0.449	−2.429±0.972	−3.19	0.761

Table 5. Operational atomic parameters e^-_{emp} found from experimental electron affinities and the corresponding e^-_{calc} values calculated using correlation (17).

Radical centre	Atom	χ_i	R^2	e^-_{emp}	e^-_{calc}	$e^-_{emp} - e^-_{calc}$
C˙	C	2.10	0.593	−0.26±0.14	0.17	−0.43
	H	2.10	0.090	−0.01±0.04	0.03	−0.04
	C(arom.)	2.45	0.449	0.60±0.06	0.38	0.22
	C(sp^2)	2.25	0.449	0.51±0.37	0.24	0.27
	Cl	3.09	0.980	2.22±0.17	1.87	0.35
	Br	2.97	1.299	2.08±0.23	2.22	−0.14
	F	3.93	0.409	1.04±0.08	1.35	−0.31
	O	3.05	0.436	−0.16±0.44	0.80	−0.96
N˙	C	2.10	0.593	−0.396±0.255	−0.39	−0.006
	H	2.10	0.090	−0.008±0.093	−0.059	0.051
	C(arom.)	2.45	0.449	0.687±0.091	0.69	−0.003
O˙	C	2.10	0.593	−0.104±0.155	0.19	−0.294
	H	2.10	0.090	0.025±0.098	0.029	−0.004
	O	3.05	0.436	−1.654±0.257	0.66	−2.314
	Cl	3.09	0.980	1.328±0.340	1.527	−0.199
	F	3.93	0.410	0.936±0.242	1.07	−0.134
	Br	2.97	1.300	1.839±0.402	1.83	0.009
	I	2.80	1.769	2.338±0.488	2.11	0.228
	C(arom.)	2.45	0.449	0.379±0.111	0.34	0.039
S˙	C	2.10	0.593	−0.41±0.386	−0.008	−0.403
	H	2.10	0.090	−0.12±0.261	−0.001	−0.121
	S	2.67	1.082	−1.84±0.457	−2.09	0.263
	O	3.05	0.436	−1.95±0.482	−1.36	−0.596
	C(arom.)	2.45	0.449	−0.02±0.236	−0.52	0.500

or nearly equal to zero, which is not always fulfilled. The e^+(H) value found statistically is markedly smaller than zero, as well as the calculated $\Delta I(CH_3)$ value.

Taft [236] was faced with similar difficulties when using the methyl group as the reference for the scale of inductive constants σ^*. There are also other factors determining the so pronounced difference between the experimental and calculated ionisation potentials of methyl radicals in the construction of a scale of radical constants. Detailed analysis of these factors is beyond the scope of this review.

When considering the e^- parameters found from the electron affinities of carbon-centred radicals, the following correlation was established:

$$e_i^- = (1.64 \pm 0.43)\chi_i R_i^2 - (3.17 \pm 1.26)R_i^2 \quad (26)$$

or

$$e_i^- = 1.64(\chi_i - 1.93)R_i^2.$$

As for ionisation potentials, this correlation permits the electron affinity parameters of carbon-centred radicals to be expressed at the atomic level on the basis of fundamental atomic characteristics, namely, electronegativities, sizes and interatomic distances

$$A_e = A_e(Me^{\cdot}) + 1.64\sum_{i=1}^{N}\frac{(\chi_i - 1.93)R_i^2}{r_i^2}. \quad (27)$$

The ionisation potentials and electron affinities of carbon-centred radicals calculated from the atomic inductive electronegativities and covalent radii are listed in Tables 6 and 7; the statistical parameters of correlations are presented in Table 8, and the operational parameters e^+ and e^- are given in Tables 4, 5.

b. Deviations from the general dependence

As noted above, the presence of substantial resonance interactions in radicals can result in deviation of their characteristics predicted in terms of the additive scheme in question from the corresponding experimental values. An alternative and, perhaps preferable, explanation of most of the deviations observed in the description of redox properties of carbon-centred radicals is that in some radicals, the carbon atom bearing the unpaired electron is not the ionisation centre.

For example, in the case of ionisation potentials, the operational atomic parameters e^+ for S, N and O atoms deviate from the linear dependence (24), and the effects of the corresponding substituents observed experimentally exceed those predicted based on the e^+ values. The experimental values of the ionisation potential I_{exp} might correspond to the I value of a heteroatom (S, N, O) present in the carbon-centred radicals and having a lone electron pair rather than to the I value of the radical centre. A similar deviation from the linear dependence has been observed in a study of the single-electron reduction potentials of arylmethylchalcogenide radical cations in aqueous solutions.[40] In addition, electron-withdrawing substituents (NO_2, CN, Hal) are able to enter into reduction processes and, hence, only for some of the carbon-centred radicals considered, do the A_e values correspond completely to the ionisation of the radical centre. For some strong electron acceptors, a saturation effect also cannot be ruled out.

Thus, most of the observed deviations of the predicted ionisation potentials and electron affinities of substituted carbon-centred radicals are most likely due to non-homogeneity of the data arrays considered. It should also be borne in mind that the ionisation potentials and the electron affinities of radicals match the energy differences between the radical and the corresponding cation in the former case and between the anion and the radical in the latter case. Hence, the energy effects of substituents described by Eqns (22) and (23) can refer both to the radical and to the corresponding ion. The positive values of e^+ and e^- imply that the radical is stabilised by the substituent in question more efficiently than the cation as compared with the $\dot{C}H_3/CH_3^+$ pair (for ionisation potentials), and that the anion is stabilised by the given substituent more efficiently than the radical, compared with the $CH_3^-/\dot{C}H_3$ system (in the case of electron affinity). Note that, the use of the notion of relative stabilisation can also imply lesser

Table 6. Ionisation potentials (in eV) of C-, S-, N- and O-centred radicals determined experimentally (I_{exp}), predicted (I_{pred}) using relation (14) and calculated (I_{calc}) from Eqns (25), (28), (30), (32).

Radical	I_{exp}	I_{pred}	$I_{exp} - I_{pred}$	I_{calc}	$I_{exp} - I_{calc}$
$MeNH\dot{C}H_2$	5.9	6.1	−0.20	8.23	−2.33
$Me(NH_2)\dot{C}H$	5.7	5.72	−0.02	7.86	−2.16
$Me_2N\dot{C}H_2$	5.7	5.74	−0.04	7.86	−2.16
$Me_2(NH_2)\dot{C}$	5.4	4.98	0.42	7.11	−1.71
$(H_2C=CH)_2\dot{C}H$	7.25	7.3	−0.05	7.73	−0.48
$Me_2(HC\equiv C)\dot{C}$	7.44	7.44	0	7.51	−0.07
(cyclo-C_5H_9)$^{\cdot}$	7	7.22	−0.22	7.38	−0.38
$HS\dot{C}H_2$	7.54	7.32	0.22	8.44	−0.91
$MeS\dot{C}H_2$	6.85	7.07	−0.22	8.19	−1.34
$H_3C^{\cdot}$	9.84	9.21	0.63	9.11	0.73
$Me_3C^{\cdot}$	6.7	7	−0.3	6.88	−0.18
$MeEt\dot{C}H$	7.25	7.41	−0.16	7.28	−0.03
$Pr^n\dot{C}H_2$	8.02	8	0.02	7.88	0.14
$Pr^i\dot{C}H_2$	7.93	7.81	0.12	7.68	0.25
$Me\dot{C}H_2$	8.12	8.47	−0.36	8.37	−0.25
$Me_2\dot{C}H$	7.37	7.74	−0.37	7.62	−0.25
$Et\dot{C}H_2$	8.09	8.14	−0.05	8.03	0.06
$HO\dot{C}H_2$	7.56	7.51	0.05	8.82	−1.25
$Me(HO)\dot{C}H$	6.85	6.77	0.08	8.07	−1.22
$MeO\dot{C}H_2$	6.9	7.13	−0.23	8.43	−1.53
$Me(MeO)\dot{C}H$	6.5	6.4	0.1	7.68	−1.18
$NC\dot{C}H_2$	9.9	9.9	0	9.18	0.72
$H_2N\dot{C}H_2$	6.29	6.45	−0.16	8.6	−2.31
$Cl_3\dot{C}$	8.06	7.99	0.07	7.82	0.24
$Cl_2H\dot{C}$	8.32	8.4	−0.08	8.25	0.07
$ClH_2\dot{C}$	8.75	8.8	−0.05	8.68	0.07
$F_3\dot{C}$	8.76	8.57	0.19	9.03	−0.27
$F_2H\dot{C}$	8.78	8.79	−0.01	9.06	−0.28
$FH_2\dot{C}$	9.04	9	0.04	9.08	−0.04
$Br_3\dot{C}$	7.5	7.59	−0.09	7.42	0.08
$Br_2H\dot{C}$	8.3	8.13	0.17	7.99	0.31
$BrH_2\dot{C}$	8.61	8.67	−0.06	8.55	0.06
$Me\dot{C}F_2$	7.92	8.05	−0.13	8.31	−0.39
$Me\dot{C}HF$	7.93	8.26	−0.33	8.34	−0.41
$H_2C=CH\dot{C}H_2$	8.18	8.25	−0.07	8.42	−0.24
(cyclo-C_3H_5)$^{\cdot}$	8.18	7.87	0.31	7.77	0.41
$CH_2=C(Me)\dot{C}H_2$	7.9	7.95	−0.05	8.11	−0.21
$(H_2C=CH)Me\dot{C}H$	7.49	7.52	−0.03	7.67	−0.18
(cyclo-C_4H_7)$^{\cdot}$	7.54	7.41	0.13	7.29	0.25
$H_2C=CHCH_2\dot{C}H_2$	8.04	8.05	−0.01	8.04	0
(cyclo-C_5H_9)$^{\cdot}$	7.21	7.11	0.1	6.98	0.23
$H_2C=CH\dot{C}Me_2$	7.13	6.78	0.35	6.93	0.2
$H_2C=CH\dot{C}HEt$	7.3	7.19	0.11	7.33	−0.03
$MeCH=CH\dot{C}HMe$	7.07	7.39	−0.32	7.54	−0.47
$H_2C=CHCH(Me)\dot{C}H_2$	8	7.71	0.29	7.69	0.31
$H_2C=C(Et)\dot{C}H_2$	7.9	7.66	0.24	7.81	0.09
$(C_6H_5)^{\cdot}$	8.32	8.31	0.01	8.46	−0.14
$Ph\dot{C}H_2$	7.24	7.24	−0.01	7.42	−0.19
$HO^{\cdot}$ (*ref*) [a]	13.017	13.04	−0.02	11.99	1.024
$HOO^{\cdot}$	11.35	11.35	0	11.45	−0.095
$ClO^{\cdot}$	10.885	10.89	0	10.84	0.048
$FO^{\cdot}$	12.78	12.78	0	12.38	0.399
$BrO^{\cdot}$	10.46	10.46	0	10.4	0.064
$IO^{\cdot}$	9.66	9.66	0	9.8	−0.137
$MeO^{\cdot}$	10.72	10.39	0.33	9.31	1.406
$EtO^{\cdot}$	9.11	9.47	−0.36	8.13	0.978
$Pr^nO^{\cdot}$	9.2	9.1	0.11	7.62	1.581
$PhO^{\cdot}$	8.56	8.56	0	8.14	0.425
$HS^{\cdot}$ (*ref*) [a]	10.429	10.43	0	10.04	0.386
$MeSS^{\cdot}$	8	8	0	8.05	−0.052
$FS^{\cdot}$	10.16	10.16	0	9.81	0.35
$MeS^{\cdot}$	9.262	9.38	−0.12	8.64	0.625
$EtS^{\cdot}$	9.6	8.92	0.68	7.93	1.673
$Pr^nS^{\cdot}$	8.2	8.73	−0.53	7.61	0.594

Table 6 (continued).

Radical	I_{exp}	I_{pred}	$I_{exp} - I_{pred}$	I_{calc}	$I_{exp} - I_{calc}$
PhS˙	8.63	8.63	0	7.82	0.81
H_2N˙ (*ref*) [a]	10.78	10.36	0.43	9.08	1.698
MeṄH	6.7	7.55	−0.85	6.7	−0.003
Me_2N˙	5.17	4.75	0.43	4.32	0.846
PhṄH	8.26	8.26	0	4.82	3.442
$H_2N-\dot{N}H$	7.61	7.61	0	7.39	0.222

[a] The reference species in the corresponding reaction series.

Table 7. Electron affinities (in eV) of C-, S-, N- and O-centred radicals determined experimentally [A_e(exp)], predicted [A_e(pred)] using relation (14) and calculated [A_e(calc)] from Eqns (27), (29), (31) and (33).

Radical	A_e(exp)	A_e(pred)	A_e(exp) − A_e(pred)	A_e(calc)	A_e(exp) − A_e(calc)
H_3C˙	0.08	0.05	0.03	0.14	−0.06
$MeC\dot{H}_2$	−0.26	−0.05	−0.21	0.21	−0.47
$MeCH_2C\dot{H}_2$	−0.07	−0.09	0.02	0.24	−0.31
$Me_2C\dot{H}$	−0.32	−0.16	−0.16	0.27	−0.59
MeEtC̈H	−0.12	−0.2	0.08	0.30	−0.42
Me_3C˙	−0.16	−0.27	0.11	0.34	−0.50
$H_2C=CHC\dot{H}_2$	0.36	0.36	0.00	0.27	0.09
$PhC\dot{H}_2$	0.91	0.62	0.29	0.49	0.42
$Ph_2C\dot{H}$	1.36	1.2	0.16	0.84	0.52
Ph_3C˙	1.56	1.77	−0.21	1.19	0.37
F_3C˙	1.84	1.76	0.08	2.27	−0.43
F_2HC˙	1.21	1.19	0.02	1.56	−0.35
FH_2C˙	0.20	0.62	−0.42	0.85	−0.65
Cl_3C˙	2.17	2.23	−0.06	1.89	0.28
Cl_2HC˙	1.58	1.5	0.08	1.31	0.27
ClH_2C˙	0.80	0.78	0.02	0.73	0.07
Br_3C˙	1.73	1.79	−0.06	1.91	−0.18
BrH_2C˙	0.82	0.63	0.19	0.73	0.09
$CF_3C\dot{F}_2$	1.81	1.76	0.05	2.26	−0.45
$MeOC\dot{H}_2$	−0.02	−0.02	0.00	0.52	−0.54
HO˙ (*ref*)	1.83	1.83	0.00	1.86	−0.03
HOO˙	1.08	1.08	0.00	2.14	−1.06
ClO˙	2.28	2.28	0.00	2.34	−0.07
FO˙	2.27	2.27	0.00	2.34	−0.06
BrO˙	2.35	2.35	0.00	2.35	0.00
IO˙	2.38	2.38	0.00	2.33	0.05
MeO˙	1.62	1.62	0.00	1.94	−0.32
EtO˙	1.72	1.72	0.00	1.98	−0.26
Pr^nO˙	1.79	1.79	0.00	1.99	−0.20
PhO˙	2.25	2.25	0.00	2.21	0.04
Pr^iO˙	1.84	1.84	0.00	2.01	−0.17
Bu^tO˙	1.91	1.91	0.00	1.96	−0.05
HS˙ (*ref*)	2.31	2.25	0.07	2.32	0.00
MeSS˙	1.75	1.80	−0.05	1.81	−0.06
MeS˙	1.87	2.12	−0.25	2.31	−0.45
EtS˙	1.95	2.05	−0.10	2.31	−0.36
Pr^nS˙	2.00	2.02	−0.02	2.31	−0.32
PhS˙	2.26	2.26	0.00	1.93	0.32
HSS˙	1.90	1.86	0.05	1.81	0.09
HOS˙	1.65	1.65	0.00	1.87	−0.22
Pr^iS˙	2.02	1.98	0.04	2.31	−0.30
Bu^tS˙	2.07	1.90	0.16	2.31	−0.24
H_2N˙ (*ref*)	0.78	0.77	0.01	0.66	0.12
MeṄH	0.45	0.60	−0.15	0.50	−0.05
Me_2N˙	0.38	0.43	−0.05	0.34	0.04
PhṄH	1.70	1.57	0.13	1.48	0.22
PhMeN˙	1.65	1.40	0.25	1.32	0.33
Ph_2N˙	2.18	2.37	−0.19	2.30	−0.12

Table 8. Statistical parameters for correlations of type (14) determined for various classes of free radicals.

Type of radicals	Series	N	R	S/ eV
C-centred	I	48	0.9768	0.2345
	A_e	20	0.9816	0.1995
S-centred	I	7	0.9278	0.6105
	A_e	10	0.8390	0.1491
O-centred	I	10	0.9938	0.3557
	A_e	12	0.9836	0.1150
N-centred	I	5	0.968	1.041
	A_e	6	0.9744	0.2179

destabilisation. In a published discussion[9–11] dealing with the influence of substituents on bond energies, similar considerations are presented concerning the situation where the effects observed can be attributed both to the RX molecule and the R˙ radical.

Equation (25) indicates that a substituent atom should have an abnormally high electronegativity ($\chi > 5.04$) to stabilise a radical more effectively than the corresponding cation. In turn, relation (27) illustrates the fact that for most of atoms ($\chi > 1.93$), stabilisation of anions predominates. Thus, it can be concluded that the described substituent effects which determine the electron potentials of free radicals refer to stabilisation of the corresponding ions. The role of steric interactions can be elucidated by comparing the adiabatic ionisation potentials, studied within the framework of the approach under discussion, with the corresponding vertical ionisation potentials.

The adiabatic potentials reflect the difference between the energies of the radicals and the cation having the most favourable (equilibrium) spatial structure, whereas vertical potentials imply identical geometries of these species. Thus, the difference between the adiabatic and vertical potentials can be attributed to structural reorganisation of a free radical caused by its oxidation.

The adiabatic and vertical potentials of the methyl radical are known to be equal. This is apparently due to the fact that both the radical and the cation are planar. The other primary, secondary and tertiary carbon-centred radicals are non-planar, unlike the corresponding cations. The difference between their adiabatic and vertical potentials remains approximately constant (0.3–0.4 eV) and does not change significantly on passing from primary to secondary or tertiary radicals, *i.e.*, the steric contribution to the adiabatic ionisation potentials is insignificant but they do contain a constant component due to the energy of spatial reorganisation. The absence of this component in the case of the methyl radical can be the main reason for the observed difference between the predicted and experimental $I(\dot{C}H_3)$ values.

The foregoing attests that steric interactions have no influence on the ionisation potentials and electron affinities of free radicals and the corresponding effect of substituents has a purely inductive nature.

It is common knowledge that cations are stabilised by electron-donating substituents and anions are stabilised by electron-withdrawing substituents. According to Eqn (15), the atomic inductive effect is proportional to the difference between the electronegativities of the given atom and the reaction centre. Hence, it is reasonable to assume that the electronegativity of the central atom (carbon) increases in the series anion < radical < cation, while the inductive effect of the substituent atoms switches from electron-withdrawing to electron-donating influence, and only in extreme cases [for example, for N(*sp*), which has $\chi_{ind} = 6.76$], is the effect of the atom adjacent to the cationic centre maintained as the electron-withdrawing influence. Thus, parameters of 5.04 and 1.93 in Eqns (24) and (26) can actually be taken as the inductive electronegativity of the reaction centre, *i.e.*, of positively and negatively charged carbon, respectively.

c. The group σ_+^C and σ_-^C scales

The empirical operational parameters e^+ and e^- established have also been used to introduce group scales called σ_+^C and σ_-^C, which make it possible to calculate the I and A_e values for carbon-centred radicals in terms of an additive scheme.[233]

$$I = I_0 + \sum \sigma_+^C$$

$$A_e = A_e^0 + \sum \sigma_-^C$$

These parameters were calculated for the most frequently encountered organic substituents with the assumption of the standard geometries and using the e^+ and e^- values for atoms contained in these substituents. These radical scales, based on electron transfer reactions and considering the substitution effect at the group level of additivity, reflect, as do the Hammett σ-constants, the overall influence of substituents on a radical reaction centre without separation of the inductive, resonance, and steric constituents. The use of group σ_+^C and σ_-^C scales simplifies the procedure of calculation of the ionisation energies of radicals and eliminates the necessity of determining interatomic distances.

Similarly, we calculated the ionisation energies of O-, S- and N-centred radicals in terms of the basic equation (14). The atomic operational parameters e^+ and e^- found in this way were then analysed using relation (16). The corresponding equations for radicals of various types are presented below in the same order which was accepted for carbon-centred radicals.[234]

d. Oxygen-centred radicals

For oxygen-centred radicals, the operational parameters e^+, which determine the relative contributions of atoms to the ionisation energy of the system, are described with high accuracy by means of atomic electronegativities and the covalent radii in accordance with Eqn (16)

$$e_i^+ = (3.94 \pm 1.01)\chi_i R_i^2 - (18.77 \pm 2.93)R_i^2$$

or

$$e_i^+ = 3.94(\chi_i - 4.76)R_i^2.$$

The corresponding atomic parameters e^- are determined in a similar way

$$e_i^- = (1.25 \pm 0.27)\chi_i R_i^2 - (2.31 \pm 0.79)R_i^2$$

or

$$e_i^- = 1.25(\chi_i - 1.84)R_i^2.$$

Thus, the ionisation energy of the alkoxy radicals $I(RO^{\cdot})$ can be presented by the relation

$$I(RO^{\cdot}) = I(HO^{\cdot}) + 3.94\sum_{i=1}^{N}\frac{(\chi_i - 4.76)R_i^2}{r_i^2}, \qquad (28)$$

and the electron affinity of oxygen-centred radicals is determined in terms of atomic parameters

$$A_e(RO^{\cdot}) = A_e(HO^{\cdot}) + 1.25\sum_{i=1}^{N}\frac{(\chi_i - 1.84)R_i^2}{r_i^2}. \qquad (29)$$

e. Sulfur-centred radicals

The atomic operational constants e^+ and e^- of sulfur-centred radicals determined from the ionisation potentials and the electron affinity correlate with the atomic electronegativities and atomic radii with a lower accuracy

$$e_i^+ = (1.71 \pm 2.19)\chi_i R_i^2 - (11.29 \pm 5.93)R_i^2$$

or

$$e_i^+ = 1.71(\chi_i - 6.61)R_i^2,$$

$$e_i^- = (-3.27 \pm 1.41)\chi_i R_i^2 + (6.84 \pm 3.68) R_i^2$$

or

$$e_i^- = -3.27(\chi_i - 2.09) R_i^2.$$

Nevertheless, the expressions obtained which relate the ionisation energies of sulfur-centred radicals to parameters of the atoms forming them appear well substantiated

$$I(\mathrm{RS}^{\cdot}) = I(\mathrm{HS}^{\cdot}) + 1.71 \sum_{i=1}^{N} \frac{(\chi_i - 6.61) R_i^2}{r_i^2}. \quad (30)$$

The electron affinity of sulfur-centred radicals is found from the relation

$$A_e(\mathrm{RS}^{\cdot}) = A_e(\mathrm{HS}^{\cdot}) - 3.27 \sum_{i=1}^{N} \frac{(\chi_i - 2.09) R_i^2}{r_i^2}. \quad (31)$$

f. Nitrogen-centred radicals

A similar correlation obtained for nitrogen-centred radicals is unsatisfactory because of the deficiency and great inaccuracy of the corresponding experimental data; therefore, the available data on the ionisation of N-centred radicals cannot serve as the base for discussion. Nevertheless, we thought it fit to present the relations determining the e^+ and e^- parameters for atoms making up N-centred radicals. As in the above cases, the electronegativities and the sizes of atoms forming the corresponding N-centred radical were used.

$$e_i^+ = (1.14 \pm 10.70)\chi_i R_i^2 - (12.01 \pm 24.9) R_i^2$$

or

$$e_i^+ = 1.14(\chi_i - 10.55) R_i^2,$$

$$e_i^- = (6.24 \pm 0.41)\chi_i R_i^2 + (13.76 \pm 0.92) R_i^2,$$

or

$$e_i^- = 6.24(\chi_i - 2.20) R_i^2.$$

The ionisation energies and electron affinities of nitrogen-centred radicals can be written as follows:

$$I(\mathrm{R_2N}^{\cdot}) = I(\mathrm{H_2N}^{\cdot}) + 1.14 \sum_{i=1}^{N} \frac{(\chi_i - 10.55) R_i^2}{r_i^2}, \quad (32)$$

$$A_e(\mathrm{R_2N}^{\cdot}) = A_e(\mathrm{H_2N}^{\cdot}) + 6.24 \sum_{i=1}^{N} \frac{(\chi_i - 2.20) R_i^2}{r_i^2}. \quad (33)$$

The ionisation potentials and the electron affinities of S-, N- and O-centred radicals calculated on the basis of the atomic inductive electronegativities and covalent radii are given in Tables 6 and 7. The electronegativities of ionic forms of the C, S, N and O atoms considered as reaction centres, obtained in accordance with the proposed procedure, are given in Table 9.

Table 9. Electronegativities and statistical parameters for correlations of type (16) determined for various types of free radicals.

Type of radicals	Parameter	χ_{rc}	N	R	S/ eV
C-centred	e^+	5.04	8 [a]	0.9509	0.266
	e^-	1.93	7 [b]	0.9502	0.328
S-centred	e^+	6.61	5	0.9368	1.3768
	e^-	2.09	5	0.8739	0.5329
O-centred	e^+	4.76	8	0.9891	0.7342
	e^-	1.84	7 [b]	0.9808	0.1975
N-centred	e^+	10.55	4	0.8393	1.9877
	e^-	2.20	3	0.9977	1.041

[a] Except for parameters for the O, N, S and N(sp) atoms; [b] except for parameters for the O atom.

The same Table contains the statistical parameters of the corresponding correlations of type (16) found for the the operational atomic parameters e^+ and e^- of the series studied.

5. The stability of free radicals in redox processes

We have already noted that the problem of radical stability, especially within the framework of the thermodynamic approaches proposed here, largely overlaps the problem of radical reactivity and is considered from the standpoint of the influence of substituents.

The stability of free radicals itself in terms of the relative energies of covalent bonds in the corresponding systems with filled electron shells is normally considered separately from the known effect of steric shielding of the unpaired electron by the molecular environment, decreasing the reactivity of the radical.[45, 114, 237] In our opinion, the concept of radical stability (reactivity) should be supplemented by one more type, namely, stability of free radicals in redox processes (subsequently referred to as redox stability).

As has already been noted, single-electron transfer is one of the most frequently encountered types of reaction in homolytic chemistry. Meanwhile, neither kinetic nor thermodynamic methods for the description of the radical effects of substituents take into account the redox stability of free radicals or provide the possibility of quantitative interpretation of the corresponding single-electron potentials. However, it is absolutely clear that the lower the ionisation potential and the higher the electron affinity of a free radical, the more easily it would enter into single-electron transfer reactions.

Thus, the redox stability of a free radical can be matched to its absolute chemical hardness (η)

$$\eta = \frac{I - A_e}{2},$$

where I and A_e are the single-electron ionisation potential and the electron affinity of the radical in the gas phase determined experimentally.

Let us consider carbon-centred radicals. Using relations (25) and (26), we express the relative chemical hardness of a carbon-centered radical (η) in terms of fundamental atomic characteristics used to describe its single-electron potentials

$$\eta(\mathrm{R}^{\cdot}) = \eta(\mathrm{Me}^{\cdot}) - 0.28 \sum_{i=1}^{N} \frac{(\chi_i - 4.22) R_i^2}{r_i^2}.$$

This relation reflects the trend of the redox stability of C-centred radicals to decrease under the influence of the vast majority of atoms present in the environment of a carbon reaction centre; only the most electronegative elements increase the $\eta(\mathrm{R}^{\cdot})$ value with respect to the chemical hardness of the methyl radical $\eta(\mathrm{Me}^{\cdot})$.

As noted above, the stability of carbon-centred radicals is often expressed as a derivative of the dissociation energy of the C–H bonds. A lower energy implies higher radical stabillity. However, a low bond energy often corresponds to a low chemical hardness of the corresponding radical. In conformity with our approach, this, conversely, implies a lower redox stability of the radical. Hence, the criteria used to describe radical stability should be chosen with caution.

6. Energies of dissociation of C–H bonds

An attractive aspect of our approach is, in our opinion, the possibility of using it successfully to describe dissociation energies of bonds E_d. We demonstrated this taking carbon–hydrogen bonds as an example.[238]

We obtained a large array of E_d(CH) values using the following relation

$$E_d(\mathrm{R_3CH}) - E_d(\mathrm{CH_4}) = \sum_i \frac{d_i}{r_{\mathrm{C}-i}^2}. \quad (34)$$

Here $E_d(CH_4)$ is the energy of the C–H bond in the methane molecule, $E_d(R_3CH)$ is the energy of the C–H bond in the corresponding derivative; the correlation parameters are: $N = 72$, $R = 0.9773$, $S = 8.484$ kJ mol^{-1}.

Equation (34) allowed high-accuracy determination of atomic constants which were designated by d and corresponded to the operational parameters e_i in the base equation (14). We were unable to determine the parameters d using the inductive and steric constituents and a correlation of type (15). Thus, the relationship between the redox and thermodynamic [expressed in terms of relative $E_d(CH)$] stabilities of free radicals remains uncertain. Nevertheless, the operational values d can be used successfully to calculate unknown energies of the C–H bonds.

IV. Conclusion

To summarise, it can be stated that the use of polar constants for the description of the reactivity and physicochemical properties of free radicals is rather limited, although in some cases, it is quite successful. The scales of specific radical constants $\sigma^{\cdot}$ are not general either. The absence of coordination between them and the ambiguity of the physical meaning of the $\sigma^{\cdot}$ radical constants might be due not only to the drawbacks of methods of their determination but rather to the limitations of principle inherent in the application of the linear methodology of correlation analysis to the free-radical chemistry and to the violation of additivity of the group influence in paramagnetic systems.

Thus, the problem of using correlation analysis in the chemistry of free radicals is far from being solved; in this respect 'homolytic' chemistry is markedly inferior to the 'heterolytic' chemistry of organic compounds. The new approaches to the quantitative description of the structure–reactivity (property) relationships for the participants of homolytic processes which we propose give hope for elimination of this objectively formed unbalance and make the quantitative organic chemistry more harmonious in some respect.

The model we developed, based on the consideration of discrete contributions of atoms, depending on the remoteness, to the substituent effects makes it possible to predict with high accuracy the quantitative characteristics of free radicals obtained experimentally. The method implies taking account of the influence of the molecular environment on the reaction centre without preliminary resolution of the effect into electronic and steric constituents. This approach provides the possibility of analysing efficiently diverse experimental results, irrespective of the nature of reaction centres.

Within the framework of our approach, we have considered only one of the three main types of free-radical processes. The quantitative description of the ionisation potentials and the electron affinities of diverse C-, N-, S- and O-centred radicals and the ionisation energies of aliphatic and aromatic amines permitted us to identify the physical nature of the corresponding substituent effects and to demonstrate the versatility of this approach in interpretation of the results of quantitative investigations in the chemistry of organic and heteroorganic free radicals.

In our opinion, of fundamental importance is the established fact that the substituent effects determining the electronic potentials of free C-, N-, O- and S-centred radicals are correlated with the stability of the corresponding ions and can be regarded as purely inductive. Nevertheless, correct quantitative determination of these values requires that the electronegativities of the ionic forms of C, N, O and S acting as the reaction centres be established.

The σ_+^C and σ_-^C scales introduced on the basis of atomic operational parameters e^+ and e^-, which determine the overall effects of substituents in single-electron transfer reactions involving C-centred radicals, exhibit high predictive capacity, although they do not clarify the physical nature of the corresponding interactions.

The approaches that we developed provide the possibility of describing a large array of dissociation energies of the C–H bonds and of determining operational atomic constants d, which are applicable for predicting unknown $E_d(CH)$ values. The notion 'redox stability of free radicals' also appears useful. It interprets this type of stability in terms of absolute hardness, without resorting to the approach according to which the relative bond energies are used as a measure of radical stability and which is criticised in the literature.

Successful use of the developed approaches for the quantitative interpretation of the ionisation energies of free radicals and molecules with closed electron shells gives hope that they would also be employed to describe the effects of substituents in other types of free-radical processes.

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