U. D. C. 541.127

Correlation Equations in Free-radical Reactions

I.B.Afanas'ev

This review deals with the methods of correlation analysis which have been applied to studies of the kinetics of free-radical reactions. It discusses the use of the Hammett and the Taft equation, of the Alfrey-Price scheme, of the Bamford equation, and also the correlations with quantum-mechanical parameters and various additive empirical methods. Polar and resonance effects in free-radical reactions are quantitatively separated by a two-parameter scheme based on the Taft equation. The relationship between the structure of the transition state and the reactivity of the free radicals is considered. 265 references.

CONTENTS

I. Introduction	216
II. Correlation with kinetic and thermodynamic parameters	216
1. The Hammett equation	216
2. The Taft equation	220
3. The Alfrey-Price and the Bamford equations	221
III. Correlation with the parameters of quantum chemistry	222
IV. Additive empirical methods of calculating the activation energies and rate constants of free-radical reactions	223
V. Separation of polar and resonance effects in free-radical reactions	223
VI. Relationship between the transition-state structure and the reactivity of free radicals	227

I. INTRODUCTION

The basic factors which determine the reactivity of free radicals towards compounds able to react with them (substrates) have already been identified. They include the polar, the resonance, and the steric effect, the dissociation energy of the bond, the type of hybridisation of the atom to which the unpaired electron is attached, etc. In general, these parameters are not mutually independent, and therefore the problems consist not so much in allowing for all the factors which may affect the reactivity of the free radical as in choosing the smallest number of such parameters which are mutually independent or approximately so.

Unfortunately, there is as yet no way of expressing the reactivity of a free radical in terms of even the three basic reaction effects (polar, resonance, and steric). Existing correlation equations apply to specific cases in which one or two of the basic effects are predominant. In the following Sections we shall discuss the correlation equations proposed by various authors for a quantitative description of the reactivity of radicals and substrates, and we shall attempt to apply the two-parameter correlation scheme to free-radical reactions.

II. CORRELATION WITH KINETIC AND THERMODYNAMIC PARAMETERS

1. The Hammett Equation

The Hammett equation - the most widely used correlation equation - was originally applied only to heterolytic reactions. This empirical relationship gives the ratio of the rate (or equilibrium) constants for the reactions of unsubstituted or substituted benzene derivatives in terms of constants[1] of the *para*- and *meta*-substituents (σ):

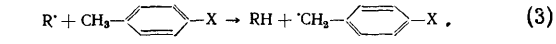
$$\lg \frac{k_{sub}}{k_0} = \rho\sigma \qquad (1)$$

where ρ is a proportionality constant. The values of σ were obtained by Hammett by comparing the dissociation constants of substituted benzoic acids. The σ constants are usually believed to characterise the polar effect of the substituent, transmitted through the σ-bond system (inductive component) and through the π-bond system (resonance component). Taft has shown[2] that when resonance involving the benzene ring can occur between the substituent and the reactive centre the Hammett σ_p and σ_m values must be corrected, or alternatively an equation of the type

$$\lg \frac{k_{sub}}{k_0} = \rho + \psi$$

must be used, where Ψ is a parameter which characterises the resonance effect, even though the use of Hammett's σ parameter as a purely polar parameter is no longer justified.

Unfortunately, in radical reactions such as the abstraction of hydrogen from ring-substituted toluenes we can expect the substituents to show an additional resonance effect, due to delocalisation of the unpaired electron in the resulting free radical:



(3)

Brown and Okamoto[3] have proposed a different set of constants for the substituents, based on their study of the rates of hydrolysis of substituted cumyl chlorides (denoted σ^+). Since tertiary carbonium ions are formed as intermediates in these reactions, the contribution of the resonance effect to σ^+ is much larger than with the normal (σ) Hammett constants. Therefore the σ^+ scale may prove very useful in studies of free-radical reactions.

a. *Application to free-radical substitution reactions*

During the 1950's it was shown that the Hammett equation is applicable (in principle) to free-radical reactions such as the abstraction of hydrogen from toluenes by bromine[4] and chlorine[5,6] atoms, the reactions of peroxide

radicals with cumene derivatives[7], radical copolymerisation reactions[8], etc. (However, most of this work is now only of historical interest, because our understanding of reaction mechanisms has become much more precise since the advent of such analytical techniques as gas–liquid chromatography and NMR spectroscopy.) Shortly after the publication of Brown and Okamoto's paper[3], Russell[9] proposed a comparison of the correlations σ and σ^+ in the study of the transition-state structure in free-radical substitution reactions of the type

$$R^{\cdot} + R'X \rightarrow RX + R''. \qquad (4)$$

According to Russell, the transition state of these reactions can be treated as the sum of two basic structures:

$$\underset{(I)}{[R^{\cdot}X : R']} \rightleftarrows \underset{(II)}{[R : \overset{\delta-}{X}\cdot\overset{\delta+}{R'}]}.$$

If the radical R$^{\cdot}$ has a high reactivity, the structure of the transition state should be (by Hammond's postulate[10]) similar to that of the reactants, i.e. the contribution of structure (I) should predominate. Conversely, in the reactions of low-activity free radicals the transition state should be similar to structure (II), since the passage of these systems over the energy barrier corresponds essentially to a weakening of the R′–X bond and therefore the structure of the transition state is similar to that of the products. Hence the rate constants of active radicals should show a better correlation with the σ parameters (since the resonance effect of R′ in structure (I) is negligible), and the rate constants of relatively inactive radicals should correlate better with σ^+ (since R′ in structure (II) has an unpaired electron, and the resonance in it should be approximately the same as in the free radical).

Hammett's equation has been used mostly in studies of free-radical substitution reactions (Table 1). As the Table shows, most of the publications deal with reactions in which hydrogen is abstracted from toluene derivatives, but Hammett's equation has been used also in studies of hydrogen abstraction from derivatives of ethylbenzene, cumene, allylbenzene, benzyl ethers, benzaldehyde, t-butylbenzene, phenols, neopentylbenzene, anisole, diphenylmethane, thiophenol and aniline, and also reactions in which iodine and chlorine are abstracted from derivatives of iodobenzene and benzenesulphonyl chloride.

Russell's hypothesis has been tested on many reactions. In 1963 Howard and Ingold[55] concluded, from a critical analysis of existing data, that for the vast majority of reactions (including those involving active radicals such as Cl$^{\cdot}$ and $(CH_3)_3CO^{\cdot}$) a more precise correlation is obtained with the σ^+ constants. However, subsequent work has produced many examples of reactions in which correlation with the σ constants is better than with σ^+ (see Table 1).

The numerical value of the proportionality constant ρ in Hammett's equation depends mainly on the structure of the transition state and on the polarity of the free radical. The effect of substituents in the substrate molecule can be expected to be smaller with structure (I) than with structure (II): in other words, ρ should decrease on going from (II) to (I) if all other factors are the same. On the other hand, any increase in the electronegativity of the free radical should increase the rate of reaction with compounds possessing electron-donating substituents. As Table 1 shows, $\rho \leqslant 0$ for all hydrogen abstraction reactions. Since in Hammett's scale the constants for electron-donor substituents are negative and those for electron-acceptor substituents are positive[1,2], it follows that all the radicals examined either show electrophilic properties in these reactions or (as in the case of $CH_3^{\cdot}$) they do not show a polar effect. However, CuCl and $C_6H_5^{\cdot}$ behave as nucleophiles ($\rho > 0$) in halogen abstraction reactions[61,62]. In keeping with this point of view, a qualitative dependence of ρ on the electronegativity of the free radicals is often observed. For example, the absolute value of ρ increases in the series $CH_3^{\cdot} < C_6H_5^{\cdot} < HOOCCH_2^{\cdot} < CCl_3^{\cdot}, Br^{\cdot}$, i.e. in the same sense as the electronegativity of these radicals. However, the dependence is not universal, since the value of ρ is determined by two factors (see above). Thus, $|\rho_{Cl}| < |\rho_{Br}|$, in spite of the fact that chlorine is more electronegative than bromine.

Table 1. Application of Hammett's equation to free-radical substitution reactions.

Radical	Substrate	Temp., °C	Solvent	ρ[a]	r[c]	ρ^+[b]	r[c]	References
$CH_3^{\cdot}$	H–$CH_2C_6H_4X$	~110	—	0	—	0	—	11
$CH_3^{\cdot}$	ditto	100	—	−0.121±0.062		−0.139±0.045		12
$CCl_3^{\cdot}$	» »	50	—	—	—	−1.46	—	13
$C_6H_5^{\cdot}$	» »	60	CCl_4	0	—	0	—	14
ditto	» »	100	ditto	−0.5[d]	—			15
» »	» »	60	» »	−0.4	—	−0.3	—	17
p-$CH_3C_6H_4^{\cdot}$	» »	60	» »	−0.1	—	−0.1	—	17
p-$BrC_6H_4^{\cdot}$	» »	60	» »	−0.32	—	−0.25	—	17
p-$O_2NC_6H_4^{\cdot}$	» »	60	» »	−0.589	—	−0.437	—	17
$HOOCCH_2^{\cdot}$	» »	130	CH_3COOH	—	—	−0.63	—	18
Cl$^{\cdot}$	» »	40	CCl_4	−0.76±0.06	—	−0.66±0.02	—	19
ditto	» »	60	C_6H_6	−0.977	0.988	—	—	20
» »	» »	80	C_6H_5Cl	−0.779	0.993	—	—	20
» »	» »	80	C_6H_5CN	−0.530	0.986	—	—	20
» »	» »	80	$C_6H_5NO_2$	−0.498	0.998	—	—	20
» »	» »	60	CCl_4	−0.480	0.997	—	—	20
$ClSO_2^{\cdot}$	» »	40	ditto	−0.56±0.02	0.98	−0.47±0.09	0.81	21
Br$^{\cdot}$	» »	80	» »	−1.68	0.945	−1.38	0.977	22
ditto	» »	80	» »	—	—	−1.23±0.13	0.970	23
» »	» »	80	C_6H_6	—	—	−1.39±0.03	—	24
» »	» »	19	» »	—	—	−1.78±0.06	—	24
» »	» »	60	» »	−0.693	0.996	—	—	20
» »	» »	80	C_6H_5Cl	−1.662	0.989	—	—	20
» »	» »	80	C_6H_5Br	−1.639	0.981	—	—	20
» »	» »	60	$C_6H_5CF_3$	−1.048	0.994	—	—	20
» »	» »	80	$C_6H_5NO_2$	−0.334	0.998	—	—	20
$(CH_3)\dot{C}O^{\cdot} + Cl^{\cdot}$	» »	40	—	−0.821±0.008		−0.695±0.015	—	25
ditto	» »	39.5	C_6H_6	−0.750	0.984	−0.599	0.953	26
» »	» »	40	CCl_4	−0.86	0.972	−0.68	0.999	27
» »	» »	40	CCl_4, C_6H_6	−0.76	0.991	−0.64	0.974	28
$(CH_3)_3CO^{\cdot}$	» »	45	$CFCl_2CF_2Cl$	−0.40	0.977	−0.35	0.989	29
ditto	» »	45	C_6H_5Cl	−0.36	0.953	−0.32	0.973	29
» »	» »	45	CH_3CN	−0.43	0.955	−0.39	0.994	29
» »	» »	40	C_6H_5Cl	−0.386	0.989	−0.345	0.999	30
$(C_6H_5)_2\dot{C}-\dot{O}$	» »	22	—	—	—	−1.16[e]	0.981	31

Table 1 (contd.)

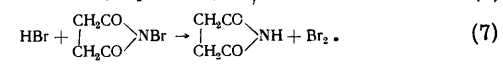
Radical	Substrate	Temp., °C	Solvent	ρ[a]	r[c]	ρ^+[b]	r[c]	References
Indoxy-phenyl	H—NHC$_6$H$_4$X	30	C$_6$H$_4$(CH$_3$)$_2$	−2.53	—	—	—	32
$(CH_2)_5\dot{N}H$·	ditto	20	H_2SO_4—CH_3COOH	−1.5	—	−1.36[e]	—	33
CCl_3·	H—CH(CH$_3$)C$_6$H$_4$X	80	CCl_4	—	—	−0.53[e]	0.98	34
Br·	ditto	80	ditto	—	—	−0.69±0.03	0.99	35
$ClSO_2$·	» »	40	» »	−0.49±0.02	0.98	−0.40±0.05	0.89	21
CCl_3·	H—C(CH$_3$)$_2$C$_6$H$_4$X	70	» »	−0.89±0.04	0.988	−0.67±0.04	0.984	36
Br·	ditto	70	» »	−0.38±0.02	0.974	−0.29±0.04	0.954	35
XC$_6$H$_4$C(CH$_3$)$_2$OO·[e]	» »	60	CH_3COOH, C_6H_5Cl	—	—	−0.41±0.01[e]	—	19
C$_6$H$_5$C(CH$_3$)$_2$OO·	» »	30	C_6H_5Cl	−0.35±0.07	—	−0.29±0.04	—	37
CCl_3·	H—CH[C(CH$_3$)$_3$]C$_6$H$_4$X	70	—	−1.24±0.05	0.960	−0.94±0.04	0.980	38
Br·	ditto	70	—	−0.96±0.04	0.942	−0.75±0.03	0.986	38
CCl_3·	H—CH(CH=CH$_2$)C$_6$H$_4$X	69.5	CCl_4	−0.58±0.03[d]	0.99	−0.39±0.03	0.94	39
Br·	ditto	69.5	ditto	—	—	−0.76±0.03	0.99	39
ditto	» »	80	» »	—	—	−0.68±0.04[e]	0.992	40
» »	H—CH(C$_6$H$_5$)C$_6$H$_4$X	80	» »	−0.93±0.04	0.991	−0.62±0.06	0.980	40
» »	То же	77	» »	−0.97	0.990	−0.72	0.973	41
» »	H—CH(COC$_6$H$_5$)C$_6$H$_4$X	80	» »	−0.92±0.02	0.997	−0.72±0.06	0.980	40
» »	H—CHXC$_6$H$_5$	77	» »	—	—	−0.246[e]	0.95	42
CCl_3·	H—CH(OCH$_3$)C$_6$H$_4$X	80	» »	—	—	−0.36[e]	0.99	43
Br·	ditto	80	» »	—	—	−0.35[e]	0.99	43
ditto	» »	40	» »	−0.48±0.04[g]	0.988	−0.43±0.03	0.995	21
» »	H—C(OCH$_3$)$_2$C$_6$H$_4$X	40	» »	—	—	−0.38[e]	0.99	43
CCl_3·	ditto	80	» »	—	—	−0.18±0.01[e]	0.99	34
Br·	H—CH(OCH$_2$C$_6$H$_5$)C$_6$H$_4$X	80	» »	−0.19	0.942	−0.12	0.947	44
C$_6$H$_5$COO·	ditto	80—90	—	−0.957±0.047	—	−0.647±0.016	—	45
Br·	H—C(C$_6$H$_5$)(OCH$_3$)C$_6$H$_4$X	80	CCl_4	—	—	0.0	—	35
CCl_3·	ditto	80	ditto	−0.20±0.02	0.947	−0.12±0.02	0.957	34
» »	H—COC$_6$H$_4$X	80	» »	−0.74	0.994	−0.67	0.951	46
CCl_3SO_2·	ditto	80	» »	−0.54±0.04	0.999	−0.46±0.03	0.979	47
$ClSO_2$·	» »	40	» »	−0.53±0.03	0.981	−0.30±0.07	0.890	48
Cl·	H—CH$_2$C(CH$_3$)$_2$C$_6$H$_4$X	70	C_6H_5Cl	−0.44±0.01[h]	0.995	—	—	49
$(CH_3)_3CO$·	H—CH$_2$OC$_6$H$_4$X	45	$CFCl_2CF_2Cl$	−0.41				50
ditto	H—OC$_6$H$_4$X	122	C_6H_5Cl	—	—	−0.74[i]	—	51
» »	ditto	122	CCl_4	—	—	−1.19[i]	—	51
	» »	24	C_6H_6	—	—	−2.72[j]	—	52
DPPH	H—OC$_6$H$_4$X	20	CCl_4	−6.4±0.3	—	−4.54±0.064[k]	—	53
DPPH	ditto	30	C_6H_6	−3.22±0.16	—	−2.77±0.09[k]	—	54
ROO·	» »	65	$C_6H_5CH=CH_2$	—	—	−1.585±0.016	—	55
$-CH_2\dot{C}H(OCOCH_3)$	» »	50	—	—	—	−1.52[e]	—	56
$(CH_3)_3CO$·	H—OC$_6$H$_2$(OC$_4$H$_9$)$_3$	122	CCl_4	—	—	−0.86[i]	—	51
ditto	» »	122	C_6H_5Cl	—	—	−0.78[i]	—	51
ROO·[l]	» »	65	—	—	—	−1.36±0.043	—	57
ROO·[m]	» »	65	—	—	—	−1.12	—	57
	H—SC$_6$H$_4$X	110	$C_6H_5CH_3$	−0.4	—	—	—	58
$-CH_2\dot{C}(CH_3)COOCH_3$	ditto	45	—	−0.23±0.1[k]	—	—	—	59
$-CH_2\dot{C}H(OCOCH_3)$	H—NHC$_6$H$_4$X	50	—	—	—	−0.6[e]	—	60
C_6H_5·	I—C$_6$H$_4$X	60	CCl_4	0.57	0.946	—	—	61
CuCl	Cl—SO_2C$_6$H$_4$X	110	CH_2=CHC_6H_5, CH_3CN	0.565	—	—	—	62

a) Correlation with σ. b) Correlation with σ^+. c) Correlation coefficient. d) Correlation with σ^0 [16]; p-NO_2 and p-CN showed large discrepancies and were not used in the calculation. e) Correlation with σ worse than with σ^+. f) p-$(CH_3)_3CO$ and p-C_6H_5O not included in the correlation. In the determination of the rate constants for hydrogen abstraction these constants had been assumed independent of the structure of X in X−$C_6H_4C(CH_3)_2OO$·, but this assumption is incorrect[37]. g) p-CH_3O not included in the correlation. h) m-NO_2 not included in the correlation. i) These values are approximate, due to the side reaction XC_6H_4O· + $HOC_6H_4Y \rightarrow XC_6H_4OH$ + ·OC_6H_4Y. j) Correlation satisfactory only for *meta*-substituents. k) Recalculated by Harvey et al.[49] 1) Oxidation of decalin. m) Oxidation of styrene. Earlier results, which were later disproved or to which substantial corrections had to be applied, are not considered in Table 1.

An accurate determination of the value of ρ can help to establish the reaction mechanism. In 1953 Kooyman and coworkers[4] suggested that succinimidyl  is formed in the reactions between bromosuccinimide and hydrocarbons, and acts as a chain carrier. They based their suggestion on the fact that the value of ρ in the Hammett equation for the bromination of substituted toluenes by bromosuccinimide was found to be −1.55, i.e. significantly different from the value −0.97 which applies to bromination by molecular bromine. On the other hand, later work showed[22-24] that the parameter ρ does not depend on the structure of the organic part of the *N*-bromoimide, and furthermore that the same value of ρ is obtained for bromination with an excess of molecular bromine. This observation suggests that the chain-propagating radical in bromination reactions with *N*-bromoimides is a bromine atom:

$$Br\cdot + RH \rightarrow HBr + R\cdot, \quad (5)$$

$$R\cdot + Br_2 \rightarrow RBr + Br\cdot, \quad (6)$$

 (7)

The lower value of ρ found by Kooyman and coworkers for reactions with molecular bromine is ascribed to the

fact that reaction (5) is reversible in the absence of excess bromine.

In 1967, the mechanism of the reaction between t-butyl hypochlorite and aromatic hydrocarbons was re-examined[29] in a similar way, because the value of ρ in reactions between substituted toluenes and $(CH_3)_3CO^{\cdot}$ radicals formed by the decomposition of di(t-butyl)peroxyoxalate was much lower than in reactions with t-butyl hypochlorite[25-28] (see Table 1). It follows that the chains are propagated mainly by chlorine atoms in the reactions with t-butyl hypochlorite. This conclusion was subsequently confirmed by Walling and McGuiness[30].

On going to more reactive substrates the absolute value of ρ decreases, as is to be expected from an increased contribution of structure (I) (see p. 218) to the transition state of the reaction†. Therefore, the reactions of $Br^{\cdot}$ and $CCl_3^{\cdot}$ with derivatives of cumene, diphenylmethane, and benzaldehyde show a better correlation with ρ than with ρ^+ [40,41,46-48].

Recently, Japanese workers have used a two-parameter Hammett equation containing the resonance constant E_R in their studies of various chain carriers—substituted cumenes in the polymerisation of styrene, *p*-chlorostyrene, *p*-methoxystyrene, methyl methacrylate[63-65,70] and substituted toluenes, benzaldehydes, and aliphatic–aromatic ketones in the polymerisation of styrene and methyl methacrylate[66-69]:

$$\lg \frac{k_{sub}}{k_0} = \rho\sigma + \gamma E_R \,. \qquad (8)$$

However, Taft himself had shown[2] that the insertion of Hammett's σ into Eqn.(8) cannot give a correct value of the resonance constant, because σ characterises the resonance as well as the polar effect of the substituent. Hence, it is better to use Taft's constants σ^0 [16] as the polar parameters in Eqn.(8), since these constants relate only to the inductive effect of the substituent.

Also, it was recently shown[28] that the methoxy group reacts with free radicals at about the same rate as the methyl group. Therefore, the rate constants of the reactions of *m*- and *p*-methoxytoluene cannot be included when correlation equations are set up for substituted toluenes. It should be noted that the point for *p*-methoxytoluene shows the greatest deviation from the line in plots[63-70] of Hammett's Eqn. (1). Lastly, deviations from Hammett's Eqn. (1) may arise from solvent effects[20] in concentrated solutions. Thus, further work is needed before the resonance constants of Eqn. (8) can be evaluated with confidence.

b. *Application to free-radical addition reactions*

During the addition of free radicals to benzene derivatives the conjugated aromatic system is converted into a cyclohexadienyl double-bond system. Therefore, Hammett's σ values (which apply to systems in which the aromatic character is not disturbed) cannot be used in this case. Furthermore, any study of reactions of this type must include, in addition to the usual assessment of the reactivity of the substrate, the partial rate constants for addition at the *para*-, *meta*-, and *ortho*- positions of each benzene derivative, because the isomeric composition of the products depends on the nature of the substituent. A full kinetic analysis of this type has been attempted only for relatively few reactions[71-75].

It has been shown that the Hammett equation is obeyed by the rate constants for the addition of the radicals $C_6H_5^{\cdot}$, $p\text{-}CH_3C_6H_4^{\cdot}$, $p\text{-}CH_3OC_6H_4^{\cdot}$, $p\text{-}ClC_6H_4^{\cdot}$, and $p\text{-}O_2NC_6H_4^{\cdot}$ to the *meta*-position, the sign changing from positive to negative on going from radicals with electron-donating to radicals with electron-accepting substituents (see Table 2). The Hammett equation can be applied also to reactions in which the radicals cyclo-$C_6H_{11}^{\cdot}$, $C_6H_5COO^{\cdot}$, $p\text{-}CH_3C_6H_4COO^{\cdot}$, $p\text{-}O_2NC_6H_4COO^{\cdot}$, $(CH_3)_2COCOO^{\cdot}$, and $C_6H_5C{\equiv}C^{\cdot}$ are added at the *para*- and *meta*-positions. However, the rate constants for the addition of aryl radicals at the *para*-position do not appear[71] to follow Hammett's equation. Ito and coworkers[71] believe that the deviations from Hammett's equation can be attributed to the resonance effect. They calculate the resonance parameters by using the fact that $\rho_{para} = \rho_{meta}$. The resonance parameters for attack in the *ortho*-position were determined in a similar way. The objections to the use of the ordinary σ constants for the substituents when the Hammett equation has a resonance term are discussed above‡.

Martin and Gleicher[76] showed that the Hammett equation is applicable to the rate constants for the addition of $CCl_3^{\cdot}$ to substituted allyl- and 3-butenylbenzenes, the proportionality constants ρ taking the values −0.29 and −0.20 respectively (Table 2). They consider these values to be too high, and they point out that the trichloromethyl radical can form complexes with aromatic substrates. Cadogan and Sadler[77] found a correlation between the rate constants for the addition of $CCl_3^{\cdot}$ and $HOOCCH_2S^{\cdot}$ radicals to substituted stilbenes and the σ^+ constants of the substituents, but this correlation was limited to a small number of olefins.

In 1948 Walling and coworkers had pointed out[8] that the rate constants for the addition of a polystyrenyl radical to ring-substituted styrenes obey the Hammett equation. Their calculations were based on the copolymerisation constants. More recently, the Hammett equation was shown to be applicable to the rate constants for the polymerisation of substituted styrenes[78]. An attempt to correlate the reactivities of ethyl-(α-substituted benzyl)-acrylates towards copolymerisation with styrene and methyl methacrylate gave a curved Hammett plot[82]. This was ascribed[82] to the resonance effect of the substituents.

In all the examples of free-radical substitution and addition reactions considered so far, the substituents are in the substrate molecules. Reactions between substituted aryl radicals and unsubstituted substrates are difficult to study. The first demonstration of the possible use of Hammett's equation for systems of this type was based[17]

† Exceptionally, the value of ρ for the reaction of $CCl_3^{\cdot}$ with derivatives of toluene[34] (−0.53) is smaller than the values for the reactions of the same radical with derivatives of cumene[36] (−0.67) and neopentylbenzene[38] (−0.94). According to Totherow and Gleicher[38], this is because the reaction of $CCl_3^{\cdot}$ is made more selective by steric hindrance in the latter two cases.

‡ Recent work has raised additional doubts about the correctness of this approach[71]. Thus, the rate constants for the addition of phenyl radicals in both the *para*- and the *meta*-position ($\rho = 0.0$) were found[73] to satisfy the Hammett equation. However, Japanese workers[80,81] find that the value of ρ in the Hammett equation for the addition of $C_6H_5^{\cdot}$ in the *para*-position depends on the method of generating the phenyl radicals. They ascribe this effect to the influence on the measured addition rate constants of the rate of the reaction

$$C_6H_5C_6H_5Y^{\cdot} + X^{\cdot} \rightarrow C_6H_4C_6H_4Y + HX$$

where the structure of X depends on the method of generating the phenyl radicals.

Table 2. Application of Hammett's equation to free-radical addition reactions.

Radical	Substrate	Product	Temp., °C	ρ	Refs.
$C_6H_5^{\cdot}$	C_6H_5X	m-$C_6H_5\dot{C}_6H_5X$	20	0.05	71
p-$CH_3C_6H_4^{\cdot}$	ditto	m-$(p$-$CH_3C_6H_4)\dot{C}_6H_5X$	20	0.03	71
p-$CH_3OC_6H_4^{\cdot}$	» »	m-$(p$-$CH_3OC_6H_4)\dot{C}_6H_5X$	20	0.09	71
p-$ClC_6H_4^{\cdot}$	» »	m-$(p$-$ClC_6H_4)\dot{C}_6H_5X$	20	−0.27	71
p-$O_2NC_6H_4^{\cdot}$	» »	m-$(p$-$O_2NC_6H_4)\dot{C}_6H_5X$	20	−0.81	71
$C_6H_5COO^{\cdot}$	» »	p-and m-$C_6H_5COO\dot{C}_6H_5X$	60	-1.61 ± 0.044^{a}	72
p-$CH_3C_6H_4COO^{\cdot}$	» »	p-and m-$(p$-$CH_3C_6H_4COO)\dot{C}_6H_5X$	60	-1.28 ± 0.047^{a}	72
p-$O_2NC_6H_4COO^{\cdot}$	» »	p-and m-$(p$-$O_2NC_6H_4COO)\dot{C}_6H_5X$	60	-2.52 ± 0.058^{a}	72
$C_6H_5C\equiv C^{\cdot}$	» »	p-and m-$C_6H_5C\equiv C\dot{C}_6H_5X$	20	−1.56	73
$(CH_3)_3CHOCOO^{\cdot}$	» »	p-and m-$(CH_3)_2CHOCOO\dot{C}_6H_5X$	60	-2.27 ± 0.03^{a}	74
cyclo-$C_6H_{11}^{\cdot}$	» »	p-and m-$C_6H_{11}\dot{C}_6H_5X$	90	1.1 ± 0.1^{b}	75
$CCl_3^{\cdot}$	$CH_2{=}CHCH_2C_6H_4X$	$CCl_3CH_2\dot{C}HCH_2C_6H_4X$	69.5	-0.29 ± 0.02^{c}	76
ditto	$CH_2{=}CH(CH_2)_2C_6H_4X$	$CCl_3CH_2\dot{C}H(CH_2)_2C_6H_4X$	69.5	-0.20 ± 0.02^{c}	76
» »	$C_6H_5CH{=}CHC_6H_4X$	$CCl_3CH(C_6H_5)\dot{C}HC_6H_4X$	105	$-0.7^{a)}$	77
$HOOCCH_2S^{\cdot}$	ditto	$HOOCCH_2SCH(C_6H_5)\dot{C}HC_6H_4X$	105	$-0.4^{a)}$	77
$-CH_2\dot{C}HC_6H_5$	$CH_2{=}CHC_6H_4X$	$-CH_2CH(C_6H_5)CH_2\dot{C}HC_6H_4X$	60	0.51	8
$-CH_2\dot{C}HC_6H_4X$	$CH_2{=}CHC_6H_4X$	$-CH_2CH(C_6H_4X)CH_2\dot{C}HC_6H_4X$	60	0.60	78
$XC_6H_4^{\cdot}$	$CH_2{=}CHC_6H_5$	$XC_6H_4CH_2\dot{C}HC_6H_5$	20	$0.95^{d)}$	79
ditto	$CH_2{=}C(CH_3)COOCH_3$	$XC_6H_4CH_2\dot{C}(CH_3)COOCH_3$	20	$0.46^{d)}$	79
» »	$CH_2{=}CHCOOCH_3$	$XC_6H_4CH_2\dot{C}HCOOCH_3$	20	$0.38^{d)}$	79
» »	$CH_2{=}C(CH_3)CN$	$XC_6H_4CH_2\dot{C}(CH_3)CN$	20	$0.35^{d)}$	79

a) Correlation with σ^{+}. b) Correlation with σ worse than with σ^{+}. c) Correlation with σ^{0}. d) ρ for the monomer minus ρ for acrylonitrile.

on the substitution reactions of *p*-methyl-, *p*-bromo, and *p*-nitrophenyl radicals with *p*-methoxytoluene ($\rho = +1$) and *p*-nitrotoluene ($\rho = +0.4$). Dickerman and coworkers[79] have shown that Hammett's equation is obeyed in reactions involving the addition of substituted phenyl radicals to styrene, methyl methacrylate, methyl acrylate, and acrylonitrile. Similarly, Yamamoto and Otsu[70] have applied the Hammett equation to the rate constants for the abstraction of hydrogen from cumene-substituted polystyrenyl radicals with different *para*-substituents, and Prokof'ev and coworkers[83] have applied it to the rate constants for the reactions of 2,6-di-t-butyl-4(4-X-phenyl)phenoxyls with t-butyl peroxide.

2. The Taft Equation

The Taft equation, which has been used to study addition reactions of aliphatic compounds, is formally similar to the Hammett equation:

$$\lg\frac{k_{sub}}{k_0} = \rho^{*}\sigma^{*}. \quad (9)$$

However, the essential difference between Eqn. (9) and the Hammett equation is that the σ^{*} constants are related exclusively to the polar effect of the substituents[2].

Until quite recently, the Taft equation had been used very seldom in studies of free-radical reactions. Taft himself quotes[84] only one example of the application of his equation to a free-radical reaction (the reaction between sodium atoms and alkyl chlorides[85]). In 1962 it was shown in the writer's laboratory[86] that the chain transfer constants in the telomerisation of ethylene with chloro- and bromochloromethane are very accurately described by Eqn. (9). (These constants, when the chain length is $n \geq 3$, are essentially the relative rate constants for the abstraction of hydrogen and bromine atoms by n-alkyl radicals, and for the removal of bromine from bromochloromethane by methyl radicals[87]). It is worth pointing out that the rate constants covered a range of 10^6, and the proportionality constant ρ^{*} lay within the range 2.33 ± 0.04 irrespective of the nature of the functional group.

We then measured the chain transfer constants for a number of other chloro- and bromochloromethanes, and refined the values previously obtained[88-90]. All the results agreed satisfactorily with Eqn. (9). We also showed that the experimental chain transfer constants for the telomerisation of ethylene with chloroform (involving breaking a C−Cl bond) and with chlorobromo- and dibromomethane (involving breaking a C−H bond) are in good agreement with the values predicted by the Taft equation.

In 1962 Patmore and Gritter[97] applied Eqn. (9) to the rate constants for the abstraction of hydrogen from derivatives of cyclohexane by the $(CH_3)_3CO^{\cdot}$ radical, but they amounted some grave difficulties. In recent years the equation has been applied to many other free-radical substitution and addition reactions (Table 3).

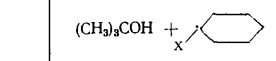
Gleicher and coworkers report[99,100] that in reactions with substituted adamantanes the inductive effect of the substituent is apparently transmitted to the reaction centre through space rather than through the carbon−carbon bond system. They calculated the relative rate constants for the reactions with $CCl_3^{\cdot}$ and $Br^{\cdot}$, using the Kirkwood–Westheimer model[102] of the electrostatic effect, and assuming that the positive charge in the transition state is unity. The calculated values turned out to be much larger than the observed rate constants, but their internal consistency was very good if the charge of the transition state was assumed to be fractional and equal to 0.12 ± 0.03 for the reactions with $CCl_3^{\cdot}$ and 0.17 ± 0.03 for the reactions with $Br^{\cdot}$. More recent work from the same laboratory[49] has confirmed that free-space transmission of the inductive effect plays an important part in the free-radical chlorination of substituted t-butylbenzenes.

In general, the rate constants of free-radical reactions should obey an extended form of the Taft equation[2]:

$$\lg\frac{k_{sub}}{k_0} = \rho^{*}\sigma^{*} + r^{*}\sigma^{r} + \delta E_s. \quad (10)$$

In this equation σ^{r} and E_S are constants for the substituents, characterising their resonance and steric effects, and r^{*}

Table 3. Application of Taft's equation to free-radical reactions.

Radical	Substrate	Product	Temp., °C	ρ^*	Refs.
$R(CH_2CH_2)_{\geqslant 3}^{\cdot}$	$H-CH_xCl_{3-x}$	$R(CH_2CH_2)_{\geqslant 3}-H + {}^{\cdot}CH_xCl_{3-x}$	70—100	2.33±0.03	86
ditto	$Br-CH_xHal_{3-x}$	$R(CH_2CH_2)_{\geqslant 3}-Br + {}^{\cdot}CH_xHal_{3-x}$	100	2.32±0.03	88—90
$CH_3^{\cdot}$	$Br-CH_xCl_{3-x}$	$CH_3Br + {}^{\cdot}CH_xCl_{3-x}$	65	2.33±0.03	86a
e_{aq}^- b	Hal—X	$Hal^- + X^{\cdot}$	20	c	91
$Cl^{\cdot}$	$H-CH_2X$	$HCl + {}^{\cdot}CH_2X$	20	−1.25	92
ditto	ditto	ditto	40	−0.85	92—94
» »	» »	» »	100	−1.00	95
» »	H—CHClX	$HCl + {}^{\cdot}CHClX$	20	−0.83	92
» »	$H-CCl_2X$	$HCl + {}^{\cdot}CCl_2X$	20	−0.49	92
$(CH_3)_3CO^{\cdot}$	$H-CH_2X$	$(CH_3)_3COH + {}^{\cdot}CH_2X$	40	−0.69	96
ditto		$(CH_3)_3COH +$ 	135	−0.43	97
$(C_2H_5)_3Si^{\cdot}$	$Cl-CCl_2X$	$(C_2H_5)_3SiCl + {}^{\cdot}CCl_2X$	80	0.29	98
$C_6H_5(CH_3)_2Si^{\cdot}$	ditto	$C_6H_5(CH_3)_2SiCl + {}^{\cdot}CCl_2X$	80	0.26	98
$CCl_3^{\cdot}$		$CHCl_3 +$ 	40	−0.40±0.04 (r=0.980)	99
$Br^{\cdot}$	ditto	$HBr +$ 	40	−0.59±0.04 (r=0.992)	100
$CCl_3^{\cdot}$	$CH_2=CHX$	$CCl_3CH_2\dot{C}HX$	69.5	−0.42 (r=0.99)	101
$-CH_2\dot{C}HC_6H_5$	$CH_2=CHCOOX$	$-CH_2CH(C_6H_5)CH_2\dot{C}HCOOX$	60	0.56	103
ditto	$CH_2=C(CH_3)COOX$	$-CH_2CH(C_6H_5)CH_2\dot{C}(CH_3)COOX$	60	0.30	104
» »	$CH_2=CHCOSH$	$-CH_2CH(C_6H_5)CH_2\dot{C}HCOSX$	60	0.28	105
$-CH_2\dot{C}(CH_3)COOX$	$CH_2=C(CH_3)COOX$	$-CH_2C(CH_3)(COOX)CH_2\dot{C}(CH_3)COOX$	30	0.70±0.18	106

a) Calculated from the results of Evans and Szwarc[87]. b) Hydrated electron. c) Published plot shows unacceptable scatter of experimental points.

and δ are the appropriate proportionality constants. Two partial expressions of Eqn. (10) are of practical importance:

$$\lg\frac{k_{sub}}{k_0} = \rho^*\sigma^* + r^*\sigma^r, \qquad (11)$$

$$\lg\frac{k_{sub}}{k_0} = \rho^*\sigma^* + \delta E_s. \qquad (12)$$

The first application of Eqn. (11) to the study of free-radical reactions was reported in an investigation[107] of the distribution of isomers in the products of the liquid-phase chlorination of aliphatic acids, esters, and nitriles. The constant ρ^* was found to be −0.212, and the hyperconjugation parameter h was also evaluated (h = 0.114, where $h = \frac{r^* \cdot \sigma^r_{CH_3}}{3}$). However, although the correlation was fairly precise, the method of calculation is open to criticism, since the authors allowed for the hyperconjugation with the methyl substituents but ignored the resonance effect of the COOH, $COOCH_3$, and CN groups. In 1965 the writer applied Eqn. (11) to the rate constants for the abstraction of iodine from alkyl iodides by alkyl radicals[108,109]. The use of the two-parameter Eqn. (11) in studies of free-radical reactions is discussed below in greater detail.

Martin and Gleicher showed[101] that the rate constants for the addition of the trichloromethyl radical to substituted olefins obey Taft's equation in its simplest form (Eqn. (9)). Similar conclusions were made for the rate constants of the addition of the polystyrenyl radical to acrylates[103], methacrylates[104], and thioacrylates[105], and also the addition of the poly(methyl methacrylate) radical to methacrylates[106], the substituents being in the alcoholic part of the monomer molecule. However, Eqn. (9) could not be applied to the rate constants of the reactions between free radicals and silicon-containing olefins of general formula $CH_2=CHSiX_1X_2X_3$[110,111], because these reactions involve large steric and resonance effects. Similarly, the rate of addition of the polystyrenyl radical to α-substituted methyl acrylates is determined mainly by the steric effect of the substituents[112].

3. The Alfrey–Price and the Bamford Equations

The Alfrey–Price[113] and the Bamford[114-116] equations were put forward to describe reactivity in radical polymerisation and copolymerisation reactions. A detailed description of these specialised branches of free-radical chemistry lies beyond the scope of the present review, and can be found in recent monographs[117-119]. We shall therefore confine ourselves to the use of the Alfrey–Price and the Bamford equation in quantitative descriptions of the reactivity of small radicals, with special reference to the recent work of Freidlina and Englin[120-123].

According to Alfrey and Price[113], the ratio of the rate constants for the polymeric radical $M_1^{\cdot}$ in copolymerisation reactions with the monomers M_1 and M_2 can be written in the form

$$r = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2}e^{-e_1(e_1-e_2)} \qquad (13)$$

where Q_1 and Q_2 are parameters which characterise the reactivity of M_1 and M_2, and e_1 and e_2 characterise the polar properties of these monomers.

Englin and Freidlina[120] proposed the use of a form of Eqn. (13), modified for chain transfer constants[124], to study the reactivity of telomeric radicals formed in the telomerisation of ethylene with carbon tetrachloride and chloroform. The Alfrey–Price scheme gives

$$C_\infty = \frac{Q_T}{Q_M}e^{-e_M(e_T-e_M)};\quad C_n = \frac{Q_T}{Q_M}e^{-e_n(e_T-e_M)} \qquad (14)$$

where C_n and C_∞ are the partial and the total chain transfer constant of the telogen; Q_M and Q_T are characteristic parameters for the reactivity of the monomer and the telogen; e_T, e_M, and e_n are the polar factors for the telogen, the monomer, and the telomeric radical of chain length n. Using Eqn. (14), Englin and Freidlina evaluated the e_n parameters for the radicals $CCl_3(CH_2CH_2)_n^{\cdot}$, where $n = 1-4$. They found that whilst the radical $CCl_3CH_2CH_2^{\cdot}$ is electrophilic ($e > 0$), the radicals with higher molecular weight acquire nucleophilic properties.

The same authors[121-123] later suggested the use of Bamford's equation[114-116]

$$\lg k_s = \lg k_{3T} + \alpha\sigma + \beta \qquad (15)$$

to study the reactivity of telomeric radicals and telogens, where k_S is the rate constant for the reaction between the radical and any substrate, k_{3T} is the rate constant for the reaction of the same radical with toluene, σ is a constant (analogous to Hammett's σ) which characterises the polar properties of the radical, and lastly α and β are constants characteristic of the substrate molecule.

For the case of chain transfer constants Eqn. (15) can be rewritten

$$\lg C_n = \sigma_n(\alpha_T - \alpha_M) + \beta_T - \beta_M. \qquad (16)$$

These equations were used to calculate σ_n for telomeric radicals in the telomerisation of ethylene, propylene, and vinyl chloride with carbon tetrachloride and chloroform. The σ_n values obtained varied in the right sense, reflecting the decrease in electrophilic character of the radicals both with increase of n and on going from vinyl chloride to ethylene and propylene.

III. CORRELATION WITH THE PARAMETERS OF QUANTUM CHEMISTRY

This review is not concerned with attempts to calculate the rate constants of free-radical reactions of the parameters of their Arrhenius equations by quantum-chemical methods. However, in addition to attempts at direct calculation of the kinetic parameters, considerable effort has been devoted to the comparison of the rate constants and activation energies of free-radical reactions with quantum-mechanical characteristics of the reactivity of the molecules and radicals. These correlations are similar in principle to those based on the use of empirical parameters (such as the constants for the substituents in the Hammett and Taft equations), but the use of quantum-mechanical parameters offers some additional advantages by giving a physical interpretation of the reactivity.

The most widely used among the quantum-mechanical correlation equations is that of Polanyi, which relates the activation energy to the enthalpy of free-radical reactions[125]:

$$\Delta E_{ac} = -\alpha\,\Delta\Delta H. \qquad (17)$$

In this equation ΔE_{ac} is the difference between the activation energies, and $\Delta\Delta H$ is the difference between the enthalpies of reactions of a given type; α is a proportionality constant. Semenov has stated[126] that this expression can be applied, to a first approximation, to the substitution reactions of most free radicals, and can be written in the form

$$E_{ac} = A - \alpha\,\Delta H \qquad (18)$$

As will be shown below (p. 228), the correctness of Eqn. (18) depends on the fact that the transition states of many free-radical reactions of the same type have very similar structures. However, in general, the proportionality constant α is a function of the reactivity of the free radical. The phenomenon has been discussed quantum-mechanically by Bagdasar'yan[119], who showed that α varies from 0 to 1 as the structure of the transition state varies from that of the reactants to that of the products.

Eqn. (17) and (18) have been applied to the abstraction of hydrogen by $CH_3^{\cdot}$ radicals ($\alpha = 0.49$ [127,128]), by Br ($\alpha = 0.86$ [129]), NF_2 ($\alpha \simeq 1$ [128]), and O ($\alpha = 0.36$ [130]). In Bagdasar'yan's calculations[119] for the reactions of $CH_3^{\cdot}$, $CF_3^{\cdot}$, and $D^{\cdot}$, α is found to be 0.38. All these examples apply to the reactions of radicals with aliphatic hydrocarbons only, because the Polanyi–Semenov equation is inappropriate[119] when the reactants contain any substituents other than alkyl groups. However, Eqns. (17) and (18) can be used in the study of reactions of a different type: for example, the abstraction of halogen atoms from alkyl halides by the $^{\cdot}SiCl_3$ radical[131], or the reactions of trifluoromethyl with halogens[132].

Zavitsas and Ehrenson[133] measured the ratio of the rate constants and the difference in the activation energies of the reactions of alkyl and cycloalkyl radicals with bromotrichloromethane and hypochlorites ($R(CH_2)_2COCl$), and evaluated the parameter α from Polanyi's equation. They found that for these radicals α is related to the stabilisation energy E_S by the expression

$$\alpha = 1.9 \cdot 10^{-3} \exp 0.28E_s. \qquad (19)$$

However, the experimental method used by these workers[133] is of doubtful validity, because recent work has shown[29,30] that appreciable amounts of chlorine are formed in reactions involving hypochlorites. Furthermore, we would have expected a linear relationship between α and E: the physical significance of the exponential relationship is not clear.

Eqns. (17) and (18) can be applied also to free-radical addition reactions[134]. Walling used[135] Eqn. (17) to determine the stabilisation energy of radicals formed during the addition of methyl radicals to vinyl acetate, vinyl ethyl ether, and methyl methacrylate.

The many "reactivity indices" which have been proposed for free-radical reactions can be divided into two groups: the parameters which define the polar (or inductive) effect, and those which define the resonance effect in reactions. In 1951 Eyring and coworkers[136] put forward a "semi-classical" approach to the evaluation of the inductive effect, based on a calculation by the MO method of the total charge on covalently bonded atoms[137]. It was shown that the free energy of the reaction between a sodium atom and chloromethanes increases in the same sense as the total charge on the chlorine atom[138]. This effect can be explained by assuming electron transfer from the sodium to the chlorine in the transition state of the reaction: increasing the number of chlorine atoms in the molecule leads to a decrease in the negative charge on the chlorine atom involved in the reaction, and hence to an increased rate of reaction. Thus, the chlorine atoms contribute a purely inductive effect. It is interesting to note that the same correlation equation applies to all the methyl halides investigated (CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, CH_3Br, CH_3I) if a correction for the different polarisabilities of the C–X bonds is applied.

Electron transfer in the transition state of the reaction between sodium and organic halides is confirmed by Wilson and Herschbach's observation of a correlation between the

electron capture coefficients and the rate constants of these reactions[139]. According to Polanyi[140], it is more correct to seek a correlation between the activation energy and the electron affinity for reactions of this type. However, both relationships point to the same mechanism.

The work of Szwarc and coworkers[141,142] bears a close similarity to the above investigations. These workers found an inverse relationship between the logarithm of the rate constants for the addition of the trifluoromethyl radical to methyl-substituted olefins and the ionisation potentials of the olefins[142]. This type of dependence is ascribed to the electron-donating properties of the methyl substituents. According to Stefani and coworkers[143] the logarithm of the rate constant for the addition of the cyclopropyl radical to olefins varies linearly with the ionisation potential of the olefins, which suggests that the cyclopropyl radical behaves nucleophilically.

In 1955 Coulson reported[144] a linear relationship between the logarithm of the rate constants for the addition of the methyl radical to aromatic compounds and the free valency index or the localisation energy of these compounds. This relationship has been widely discussed in the literature. The quantum-mechanical significance of these correlations has been considered in detail in monographs[119,145], and the work of Szwarc and coworkers up to 1958 is fully reviewed by the authors themselves[146]. The localisation energy of one of the π-electrons on the reactive centre decreases if the second electron can conjugate with the substituents of an unsaturated compound. Therefore, the correlation of the rate constants or activation energies with the localisation energies is evidence for the presence of a large resonance effect in these reactions.

Later work has revealed correlations between the localisation energies and the rate constants (and activation energies) for the reactions of the trifluoromethyl and the trichloromethyl radical with aromatic compounds[147,148], of hydrogen atoms with olefins[149] and hydrocarbons[150], and of the ethyl radical with olefins[151]. Chlenov and Basilevskii[152] studied the relationship between the rate constants for the reactions of the methyl, trifluoromethyl, and trichloromethyl radicals with aromatic compounds and the stabilisation energy, defined as the difference between the π-energies of the delocalised transition state and of the reactants. According to these workers, correlation with the stabilisation energy is more satisfactory than with the localisation energy when a large polar effect is present. Unruh and Gleicher[153] obtained a good correlation (correlation coefficient 0.977) between the rate constants for the abstraction of hydrogen from methyl-substituted aromatic compounds by the trichloromethyl radical and the difference between the π-bond energies of the resulting radical and of the reactant, calculated by the SCF LCAO MO method.

IV. ADDITIVE EMPIRICAL METHODS OF CALCULATING THE ACTIVATION ENERGIES AND THE RATE CONSTANTS OF FREE-RADICAL REACTIONS

Additive schemes for calculating by empirical methods the rate constants (and particularly the activation energies) of free-radical reactions have recently been developed to a remarkable degree. The activation energies of the logarithms of the rate constants are treated as empirical functions of a number of parameters which characterise the substrates and the radicals. Though similar to the correlation equations of the Hammett–Taft type, these methods differ essentially from those equations because the parameters on which they rely are not determined by reaction effects (polar, resonance, or steric), but by some specifically chosen components of the energy of the activated complex. The activation energies of radical reactions are treated as functions of the dissociation energies of the "activated" forms of the broken bond and the newly formed bond (i.e. the bonds in the activated complex[154]), expressed as sums of energy terms for the pair interactions of atoms in the activated complex[157], and also as functions of the dissociation energies of the real broken bond and of the newly formed bond[156]. §

These methods have been discussed in detail in a number of review articles, [154–156] and therefore we shall not dwell on them, except for the following observation. There can be no doubt of the reality of the various empirical relationships which have been reported. However, it is exceedingly difficult to define the region over which such relationships apply. Thus, Moin assumes[154] that in any free-radical substitution reaction

$$R^{\cdot} + R'X \rightarrow [R \ldots X \ldots R'] \rightarrow RX + R'^{\cdot} \qquad (20)$$

the dissociation energy of X...R′ in the activated complex is independent of the structure of the attacking radical R·. But this assumption is inconsistent with Hammond's postulate[10] that the structure of the activated complex (i.e. the transition state), and therefore also the dissociation energy of the X...R′ bond, varies from a structure close to that of the reactants (for very reactive R radicals) to a structure close to that of the reaction products (for relatively inactive R radicals).

Moin[154] correctly states that his relationships between activation energies and the dissociation energies of the bonds in the activated complex are similar to the Polanyi–Semenov equation. Hence, the regions of applicability of the two equations should be the same. However, the Polanyi–Semenov equation is applicable only to the reactions of radicals with aliphatic hydrocarbons, in which structurally uniform activated complexes[119] are formed.

V. SEPARATION OF POLAR AND RESONANCE EFFECTS IN FREE-RADICAL REACTIONS

In this Section we shall discuss the application of the two-parameter Taft equation

$$\lg \frac{k_{sub}}{k_0} = \rho^{\cdot}\sigma^{\cdot} + r^{\cdot}\sigma^{r} \qquad (11)$$

to the study of the reactions of free radicals with compounds whose substituents show both polar and resonance effects. Clearly, Eqn. (11) is applicable only if the steric effect of the substituents is negligible.

In contrast to ordinary substitution reactions, whose transition state contains a formally quinquevalent carbon atom (as in the S_N2 reactions, for example), free-radical substitution reactions proceed through a transition state with little steric hindrance:

$$Y^- + CR_1R_2R_3X \rightarrow \left[\begin{array}{c} R_1 \quad R_2 \\ Y \ldots C \ldots X \\ \quad | \\ \quad R_3 \end{array}\right]^- \rightarrow YCR_1R_2R_3 + X^- \quad S_N2 \text{ mechanism}, \qquad (21)$$

$$Y^{\cdot} + CR_1R_2R_3X \rightarrow [Y \ldots X \ldots CR_1R_2R_3] \rightarrow YX + {}^{\cdot}CR_1R_2R_3 \quad \text{Free-radical substitution mechanism}. \qquad (22)$$

§ A new method of calculating the activation energy of free-radical reactions, based on a presentation of the potential energy of the reacting system in terms of Morse curves, has recently been suggested[157,158].

Therefore, the steric effect can often quite correctly be ignored. However, in the presence of several substituents we must consider a special form of the steric effect, in which resonance in the transition state is geometrically precluded. In the following calculations we shall confine ourselves, as a rule, to the rate constants of monosubstituted compounds, with the exception of methyl and halogen substituents.

Only the polar constants (σ^*) of Taft's equation[2] were available in the literature. Therefore, one particular series of free-radical substitution reactions (the reactions of primary alkyl radicals in the liquid phase) was used to calculate the resonance constants σ^r of the substituents by Eqn. (11). As stated above (p. 220), the chain transfer constants $C_{\geqslant 3}$ in the telomerisation of ethylene with halogenomethanes obey the Taft equation in its simplest form (Eqn. (9)), the proportionality constant ρ^* having the value 2.33 to a first approximation irrespectively of the nature of the atom abstracted (H, Cl, or Br). Hence, σ^r was determined from the chain transfer constants $C_{\geqslant 3}$ of monosubstituted derivatives of methane with substituents showing both polar and resonance effects. It was assumed that for this reaction $\rho^* = r^* = 2.33$. This assumption is undoubtedly arbitrary, but it seemed a reasonable one because it yields a single scale for the quantities σ^* and σ^r. However, it must be borne in mind that whereas a change in r^* will produce a change in the absolute value of σ^r, their relative values will remain unchanged. Thus,

$$\sigma^r = \frac{1}{2.33} \lg \frac{C_{sub}}{C_0} - \sigma^*. \qquad (23)$$

The measured chain transfer constants $C_{\geqslant 3}$ for the telomerisation of ethylene with methyl, ethyl, and isopropyl iodide[108,109], 1,1-dichloroethane[89], bromoacetic acid[159], toluene, acetone, acetic acid, and acetonitrile[160] (at 100°) were inserted into Eqn. (23), and also the chain transfer constants for the polymerisation of ethylene with methanol and propylene (at 130° and 1350 atm), obtained by Mortimer[161]. (Although these latter data were obtained at a higher temperature, the effects of temperature and pressure increase can be expected to be mutually compensating to a large extent.)

The results of our calculations are shown in Table 4. The value of $\sigma^r_{CH_2COOH}$ adopted is the average of the values calculated from the chain transfer constants for acetic and bromoacetic acid. The resonance constants of the alkyl substituents were calculated from the chain transfer constants of alkyl iodides. $\sigma^r_{CH_2CH_3}$, found from the chain transfer constant of 1,1-dichloroethane ($C_3 = 0.178$), is practically the same as the value obtained from $C_3^{C_2H_5-I}$.

The resonance effects of the substituents in the substrate molecule which reacts with a free radical are probably determined mainly by the delocalisation of the unpaired electron onto these substituents in the transition state of the reaction. There is nothing new, essentially, in this point of view. The interaction of the unpaired electron with substituents in free radicals has been demonstrated many times. Thus, it has been shown that the stabilisation energy of benzyl radicals is increased by the presence of alkyl substituents[162]. Gilbert and Kreilick[163] have calculated the distribution of the unpaired electron density in substituted phenoxy radicals. They found that the delocalisation of the unpaired electron increases when the substituents $CH_2COOC_2H_5$, $C(CH_3)_3$, and CH_3CO are introduced in the *para*-position.

Furthermore, the distribution of unpaired electron density has a significant effect on the reactivity of the free radical. Thus, the rate of reaction of the methyl radical at the *ortho*-position, the *para*-position, and the oxygen atom of the phenoxy radical depends on the distribution of spin density in the latter radical[164]. Similarly, a relationship has been found between the unpaired electron density distribution in phenoxy and aryloxy radicals and the activation energy of their reactions with t-butyl peroxide[165,166].

Table 4. Resonance constants of the substituents (σ^r) and spin densities in the resulting free radicals (p_R).

R–X	$C_{\geqslant 3}$ (100°)	σ^{*a}	σ^r	p_R
CH_3–I	4.5 [109]	0	0	1.000
CH_3CH_2–I	14.8 [109]	−0.10	0.32	0.919 [167]
$(CH_3)_2CH$–I	48.3 [109]	−0.20	0.64	0.844 [167]
CH_3–H	$1.5 \cdot 10^{-6}$ [a] [86]	0	0	1.000
$HOOCCH_2$–H	0.0037 [160]	1.05	0.40	0.923 [168]
CH_3–Br	0.0025 [a] [159]	0	0	1.000
$HOOCCH_2$–Br	3.7 [159]	1.05	0.31	0.923 [168]
$NCCH_2$–H	0.0283 [160]	1.3	0.54	0.852 [169]
$C_6H_5CH_2$–H	0.0254 [160]	0.215	1.605	0.621[c]
CH_3COCH_2–H	0.0290 [160]	1.12[c]	0.72[c]	0.830 [170, 171]
CH_2=$CHCH_2$–H	0.015 [b] [161]	0.1	1.62	0.604 [172]
$HOCH_2$–H	0.0021 [b] [161]	0.555	0.795	0.840 [169]
CH_3OCH_2–H		0.520	0.97[c]	0.770 [173]
$C_6H_5OCH_2$–H		0.85	0.66[d]	0.848[c]
CH_3CO–H		1.65	1.15[d]	0.728[c]

a) Calculated value. b) Chain transfer constants in the polymerisation of ethylene at 130° and 1350 atm. c) Obtained by Eqn. (25). d) Obtained from the rate constants for the methyl radical reactions (Table 5) by Eqn. (11).

The delocalisation of the unpaired electron on the substituents of the substrate molecule in the transition state of a free-radical reaction can be compared with the spin-density distribution in the resulting free radical. These ideas were developed by Dixon[174]. However, he points out that direct comparison of spin-density distribution in the radicals with the reactivity of the reacting molecules is impossible, because radicals (unlike molecules) have a planar structure. Therefore, Dixon prefers to use the spin–spin interaction constants of vicinal protons to characterise the delocalisation of electron spin in the transition state. Nevertheless, the transition state for radical substitution reactions involving monosubstituted compounds hardly ever presents geometrical restrictions to the delocalisation of the unpaired electron on the substituent. Hence, we believe that the resonance effect of substituents can be directly related to the spin density in the radicals (calculated from ESR spectra).

We have used spin-density values obtained from the most accurate form of the McConnell equation for the hyperfine structure (HFS) constants of the protons in the methyl groups of the $CH_3\dot{C}HX$ radicals[167,169]:

$$p_R = \frac{a^{CH_3}}{29.3\,(1 - 0.081)}. \qquad (24)$$

In this equation, p_R is the spin density at the α-carbon atom of the $XCH_2^{\cdot}$ radical, a^{CH_3} is the HFS constant of the freely rotating methyl group of the $CH_3\dot{C}HX$ radical, the factor $(1 - 0.081)$ allows for the delocalisation of the unpaired electron on the CH_3 group[167]. (The traditional

symbol ρ for the spin density has been replaced by p_R to avoid confusion with the proportionality constants ρ and ρ^* of the Hammett–Taft equations.) Values of p_R are listed in Table 4.

We have tried to establish a relationship between the resonance constants σ^r of the substituents, calculated by Taft's Eqn. (11), and the spin density on the substituents in the resulting free radicals, in the form of the equation[175-177]:

$$\sigma^r = b(1 - p_R). \quad (25)$$

Eqn. (25) was solved for the σ^r and p_R values of the radicals $CH_3^\cdot$, $CH_3CH_2^\cdot$, $(CH_3)_2CH^\cdot$, $HOOCCH_2^\cdot$, $NCCH_2^\cdot$, $CH_2{=}CHCH_2^\cdot$, and $HOCH_2^\cdot$. The result, obtained by least squares, was

$$\sigma^r = (4{,}23 \pm 0{,}48)(1 - p_R), \quad \text{correlation coefficient } 0.988. \quad (26)$$

This expression can be used to calculate new values of σ^r and p_R, and other derived quantities. Thus, we obtained $\sigma^r_{CH_2COCH_3} = 0.72$, $\sigma^r_{CH_2OCH_3} = 0.97$, and $\sigma^r_{CH_2C_6H_5} = 0.621$. Since the chain transfer constant for the telomerisation of ethylene with acetone is known ($C^{CH_3COCH_3}_{\geqslant 3} = 0.0290$, Table 4), it follows that $\sigma^r_{CH_2COCH_3}$ can be found in the same way as the other resonance constants: from Eqn. (11) and the known polar constant $\sigma^*_{CH_2COCH_3} = 0.60$.[2] However, this method of calculation gives the anomalously high value $\sigma^r_{CH_2COCH_3} = 1.24$. Therefore, we prefer to use a different value of $\sigma^*_{CH_2COCH_3}$ for free-radical processes. Inserting $\sigma^r_{CH_2COCH_3} = 0.72$ into Eqn. (11) we obtain $\sigma^*_{CH_2COCH_3} = 1.12$. As we shall show below, the new value of $\sigma^*_{CH_2COCH_3}$ can be used with advantage in the study of other free-radical reactions.

The spin-density distribution in the benzyl radical has been determined theoretically by several workers, but the value of $p_{CH_2C_6H_5}$ depends very appreciably on the method of calculation (see, for example, Ref. 178). Inserting into McConnell's Eqn. (24) the value $p_{CH_2C_6H_5} = 0.621$ found by Eqn. (26), we can find a^{CH_3} for the ESR spectrum of the $C_6H_5\dot{C}HCH_3$ radical: $a^{CH_3} = 29.3\ (1 - 0.081)p_{CH_2C_6H_5} = 16.8$ G. It is interesting to note that in a recent paper[179] the HFS constants $a^H = a^{CH_3} = 16.5$ G are proposed for the $C_6H_5\dot{C}HCH_3$ radical.

The Taft equation with polar and resonance terms (Eqn. (11)) can be applied to the reactivity of monosubstituted methane derivatives towards free radicals. All the data available at the time of writing are collected in Tables 5 and 6. We have included only those radicals for which more than four rate constants were known. This gave at least four equations to be solved for evaluating the results by least squares. Since the chain transfer constants of polymeric radicals are the least accurately known, only the constants obtained in the polymerisation of vinyl acetate were considered, because this reaction has been fully characterised. As the Table shows, three correlations were obtained for five reaction rate constants involving the radicals $CH_3(CH_2)_2\dot{C}H(CH_2)_2CH_3$, $HO^\cdot$, $Na^\cdot$: one for six values ($I^\cdot$), one for eight values ($CH_3^\cdot$), one for nine values (polyvinyl acetate radical), and two for ten values ($CF_3^\cdot$ and $C_6H_5^\cdot$).

Table 5. Application of Taft's Eqn. (11) to the rate constants of reactions between free radicals and R–H compounds.

R–H	Rate constants in the gas phase (g.p.) and liquid phase (l.p.)							
	$X(CH_2CH_2)_n^\cdot$ $C^a_{\geqslant 3}$ l.p. 100°	$CH_3^\cdot$ $k\cdot10^{-8}$, g.p. 100° $cm^3\ mole^{-1}\ s^{-1}$	$CH_3(CH_2)_2\dot{C}H(CH_2)_2CH_3$ $C^3_{\geqslant 3}$ l.p. 100°	$CF_3^\cdot$ $k\cdot10^{-8}$, g.p. 100° $cm^3\ mole^{-1}\ s^{-1}$	$\frac{k}{k_{CCl_4}}$ $C_6H_5^\cdot$ l.p. 60°	$HO^\cdot$ [b] $k\cdot10^{-11}$ l.p. $cm^3\ mole^{-1}\ s^{-1}$ 20°	$I^\cdot$ $k\cdot10^{-4}$ g.p. $cm^3\ mole^{-1}\ s^{-1}$	$X(CH_2\dot{C}H)_n$ $\lvert$ $OCOCH_3$ $C^a\cdot10^4$ l.p. 60°
CH_3–H	c	0.0019[180]	$3.9\cdot10^{-6}$ [h, i]	0.36[d 198–200]	0.005[h, i]	0.07[h, i]	0.0025[217]	k
$ClCH_2$–H				0.83[200]	0.07[14]			
Cl_2CH–H			0.25[196]	5.54[201]	0.48[14]			4[221]
Cl_3C–H			9.6[196]	17.7[d 199, 201]	3.2[14]	0.074[211]		140[221–223]
$BrCH_2$–H				0.70[200]				
$HOCH_2$–H		0.23[d 181, 1 2]		18.6[202, 203]	0.13[14]	5.36[d 212–215]	0.40[218]	6[221]
$HOOCCH_2$–H		0.15[e 183]			0.086[14]	0.166[212, 215]		10[221]
$NCCH_2$–H		0.90[184]						10[221]
CH_3COCH_2–H		0.65[d 180, 185[c], 187]	0.125[197]	5.47[204]	0.17[14]	0,64[d 211, 212, 215]		19[d 222, 224]
CH_3OCH_2–H		0.62 [d, g 182, 185, 189]		52.5[205]	0.28[14]		5.8[218]	
CH_3CO–H		33.1[g 190]		243[206]	2.4[208]	5.13[j]	520[218]	420[d 221, 223–225]
$C_6H_5OCH_2$–H		0.35[g 191]	0.14[197]		0.07[20]			10[196]
$CH_2{=}CHCH_2$–H		1.33[d 185, 192]					56[219]	
$C_6H_5CH_2$–H		1.16[d 185, 188, 193–195]	1.24[197]	135[207]	0.33[d 17, 210]		25[220]	25[d 221, 222, 224, 226]
ρ^*	2.33	1.51±0.14	2.70±0.53	0.56±0.14	1.11±0.07	0.01±0.20	1.67±0.32	1.02±0.16
r^*	2.33	1.51±0.14	2.22±0.26	1.55±0.05	0.90±0.13	1.62±0.34	3.13±0.24	1.21±0.12
r			0.962	0.994	0.936	0.959	0.952	0.968

a) Chain transfer constants. b) Rate constants for the reactions of $HO^\cdot$ at pH 7 were chosen for the calculation, because hydroxyl radicals are converted into $O^\cdot$ in alkaline media[231]. c) These values of chain transfer constant were used to calculate σ^r (see Table 4). d) Mean value. e) Reaction with CH_3COOCD_3. f) All these rate constants were recalculated using a corrected value[186] for the rate constant of the recombination of methyl radicals (2.3×10^{13} $cm^3\ mole^{-1}\ s^{-1}$). g) The rate constants for the reactions of methyl radicals were used to calculate the corresponding σ^r. h) Calculated from Taft's Eqn. (11). i) Chloroform taken as standard compound. j) Obtained from $k_{CH_3CHO}/k_{CH_3OH} = 2.25$[216] and $k_{CH_3OH} = 5.36\times10^{11}$ $cm^3\ mole^{-1}\ s^{-1}$. k) Toluene taken as standard compound in Eqn. (11).

All the available data (except a few doubtful ones) were used to analyse the rate constants of the gas-phase reactions of the methyl radical. For example, the results of Raal and Steacie for the reactions of $CH_3^{\cdot}$ with halogenomethanes were not included, because hydrogen halides are formed in these reactions[227-229]. As Table 5 shows, the rate constants for the reactions of methyl radicals are fitted by Eqn. (11) for the special case of $\rho^* = r^* = 1.51 \pm 0.14$. This is not unexpected, since the constant r^* had been taken to be equal to ρ^* for the reactions of alkyl radicals in the liquid phase. Calculations by Eqn. (11) with $\rho^* \neq r^*$ confirmed that these quantities cannot differ by more than 0.17 of a unit of ρ^* for the reactions of methyl radicals. From this correlation expression, and the known rate constants for the reactions of the methyl radical with anisole[191] and acetaldehyde[190], we obtain $\sigma^r_{CH_2OC_6H_5} = 0.66$ and $\sigma^r_{COCH_3} = 1.15$, and also $p_{CH_2OC_6H_5} = 0.848$¶ and $p_{COCH_3} = 0.728$. These resonance constants have been used to set up correlation expressions for other free radicals.

Table 6. Application of Taft's Eqn. (11) to the rate constants of the reactions of sodium atoms with R–Cl compounds.

Rate constant	$(CH_3)_3CCl$	$(CH_3)_2CCl_2$	CH_3CCl_3	CCl_4	$CH_2=CHCH_2Cl$	ρ^*	r^*	r
$k \cdot 10^{-11}$ (Ref. 232) cm^3 mole^{-1} s^{-1} at 247°, g.p.	2.76	42.3	393	2260	27.3	1.234 ±0.007	0.760 ±0.016	0.9996

The correlation expressions for the reactions of other free radicals were obtained in a similar way. The rate constant for the reaction of the phenyl radical with acetonitrile[14] was not included in the calculation because it showed a serious discrepancy, probably associated with the experimental errors inherent in the chosen method[17] of measurement of k. In the study of the reactions of the hydroxyl radical in aqueous solutions the rate constants of the reactions with methane and acetonitrile[214] were excluded from the calculation because the measurements had been made at pH 9, i.e. under conditions where the radical anion $O^{\cdot-}$ is also present[231].

It is evident from Tables 5 and 6 that our correlation expressions have an accuracy of 10–25% for ρ^* and 10–15% for r^*. The only exception is the value of ρ^* for the reactions of the trifluoromethyl radical, which lies within the range from –0.20 to +0.20. These errors are fairly large, but all the correlation coefficients (except for one value of 0.936 for the reactions of the phenyl radical) are greater than 0.950, and two of them are greater than 0.990. Thus, we may conclude that the correlation is entirely satisfactory†.

We must stress that these calculations were made with data from different sources and having different precision. Furthermore, the rate constants of free-radical reactions can seldom be measured to an accuracy of better than 50%. Also, the number of available data was so small that it was not always possible to exclude values of doubtful reliability from the calculation. Hence, the correlation errors are relatively large at this stage, but we think it likely that the correlation will improve when a larger fund of accurate experimental data becomes available.

A qualitative dependence of ρ^* on the electronegativity of the free radicals can be observed for reactions of a given type (ignoring temperature differences and different reaction media). It is found that ρ^* decreases in the sequence

$$X(CH_2CH_2)^{\cdot}_n,\ CH_3(CH_2)_2\dot{C}H(CH_2)_3CH_3 > CH_3^{\cdot},\ I^{\cdot} > C_6H_5^{\cdot} > CF_3^{\cdot} > HO^{\cdot}.$$

In this series the electronegativity of the radicals increases from left to right. The value of r^* should be independent of the polar properties of the radicals, and should be determined only by the structure of the transition state of the reaction. The dependence of r^* on the structure of the transition state is discussed again below.

The effect of the statistical factor has been ignored in all the above calculations. "Intuitively", the statistical factor should be equal to the number of equally probable centres of attack of the reagent (for example, the free radical) on the substrate molecule. Benson[234] has tried to develop the concept of a statistical factor from the theory of absolute reaction rates. He has shown that it is not obvious, in general, that the "intuitive" statistical factor can be identified with a factor giving the symmetry numbers in the theoretical rate constant equation. Studies of reactions involving the hydrogen atom[235,236] have shown that the real statistical factor, calculated from the ratio of the pre-exponential terms in the rate constants for the reactions, is not the same as the factor given by "intuitive" considerations. It should be noted that a one-sided calculation of the statistical factor is objectionable also from general considerations, since other, "non-chemical" contributions to the rate constant must be taken into account (for example, the effect of moments of inertia[236]).

¶ Hudson and Root[230] have recently obtained the value $p_{CH_2OCH_3} = 0.831$ by using Eqn. (24) in conjunction with ESR data.

† Migita and coworkers[233] conclude, by comparing the rate constants for the chlorination of chloroalkanes and chlorosilanes, that the resonance effect of chlorine atoms in the α-position to the reaction centre is greater than the hyperconjugation effect of the C–H and C–C bonds. We observe that these workers' rate constants for the chlorination of chloroalkanes and nitriles[92-94,233], obey Taft's Eqn. (11) with $\rho^* = -3.54 \pm 0.28$ and $r^* = 1.27 \pm 0.40$ (at 40°) except for compounds with chlorine atoms in the α-position to the reaction centre. If the rate constants for the chlorination of chloroalkanes with chlorine atoms in the α-position are inserted into this equation, the accelerating effect of chlorine as an α-substituent is found to correspond to $\sigma^r_{CH_2Cl} = 1.5$ and $\sigma^r_{CH_2Cl} = 3.2$. (We note that σ^r for a classical resonance-inducing substituent such as $-CH_2CH{=}CH_2$ is 1.62 (Table 4)). Therefore, we suggest that the effect of chlorine atoms as α-substituents on the rate of chlorination of chloroalkanes should be ascribed not to the resonance effect of chlorine, but to some other effect (for example, the change in hybridisation of the carbon atom).

Nevertheless, all the correlation expressions obtained (as well as some published data[98]) were recalculated to allow for the statistical factor: the effect on the results was negligible within the quoted error limits. In four cases the correlation was more satisfactory without the statistical factor, in four cases the correlation was improved by the statistical factor, and in one case the statistical factor had no effect. None of the effects was large.

Steric preclusion of resonance

As already pointed out (p. 224), the presence in the substrate molecule of several substituents exhibiting a resonance effect can lead to a spatial disturbance of the conjugation of the unpaired electron with the substituents in the transition state of the reaction. Steric preclusion of the resonance was observed in a number of systems, for example in studies of the addition of a methyl radical to unsaturated and to aromatic compounds.[146]

In our calculations of the resonance constants of the ethyl and the isopropyl radical from the chain transfer constants of these radicals in the telomerisation of ethylene with alkyl iodides we found (Table 4) that the resonance effect of two methyl groups is equal to twice the effect of a single methyl group ($\sigma^r_{CH(CH_3)_2} = 0.64$, $\sigma^r_{CH_2CH_3} = 0.32$). This was confirmed by measuring the chain transfer constants in the telomerisation of ethylene with ethyl bromide and isopropyl, and also by inserting the σ^r values obtained into the correlation equations. Hence, no steric preclusion of resonance occurs in radical substitution reactions when a second methyl group is introduced into the substrate molecule.

However, a study by the competitive method of the reactivity of the compounds $CH_3COOH - ClCH_2COOH - CH(COOH)_2$ and $BrCH_2COOH - BrClCHCOOC_2H_5 - BrCH(COOC_2H_5)_2$ has shown that the introduction of chlorine or a second carboxyl into a molecule of acetic or bromoacetic acid increases the chain transfer constant by a factor of 35–25 and 14–4 respectively[159,177]. Using Taft's equation it is readily shown that the reactivity of these compounds can be expressed as the overall effect of the CHClCOOR group (with R = H or C_2H_5), $\Sigma\sigma^* = 1.86-2.10$, and of the group $CH(COOR)_2$, $\Sigma\sigma^* = 1.64-2.06$. (By analogy with other reactions of n-alkyl radicals the proportionality constant is taken to be $\rho^* = 2.33$). Although the polar constants σ^* of these groups are unknown, we can establish that the observed overall effects of the CHClCOOR and $CH(COOR)_2$ groups are almost fully accounted for by the polar effect, noting that $\sigma^*_{CH_2COOH} = 1.05$ [2] and allowing for the "saturation effect" in the summation of the inductive constants (for example, $\sigma^*_{CH_2Cl} = 1.05$, $\sigma^*_{CHCl_2} = 1.94$, $\sigma^*_{CCl_3} = 2.65$). Thus, in these cases the preclusion of resonance is almost total.

VI. RELATIONSHIP BETWEEN THE TRANSITION-STATE STRUCTURE AND THE REACTIVITY OF FREE RADICALS

In the applications of Taft's two-parameter Eqn. (11) to studies of the reactions of alkyl radicals with alkyl bromides and iodides[109,159], and also of the reactions of sodium atoms with alkyl chlorides (Table 6), methyl groups were examined among other substituents. It was found that the effect of methyl groups, like that of the other substituents, can be resolved into a polar and a resonance component. However, in the more general case the influence of alkyl groups in free-radical reactions cannot be described in terms of these two effects alone.

Deviations from Eqn. (11) in the case of methyl substituents are observed in the reactions of free radicals with aliphatic hydrocarbons. The effect of methyl groups on the rate of hydrogen abstraction by radicals from methane, ethane, and propane could have been expected to be additive, as is found for example in the reactions of radicals with methyl-, ethyl-, and isopropyl halides with C–X bond breaking[109,159]. However, as Table 7 shows, the increase in reaction rate for all radicals is much greater on going from methane to ethane than from ethane to propane. Thus, the Taft equation (Eqn. (11)) cannot be applied to these reactions, since the quantities ρ^* and r^* are a function of R′ in the reactions

$$R^{\cdot} + H{-}R' \rightarrow RH + R'^{\cdot} \quad [R' = CH_3, CH_2CH_3, CH(CH_3)_2]. \qquad (27)$$

The writer has shown[237] that a direct proportionality exists between $\lg(k_{C_2H_6}/k_{CH_4})$ (see Table 7) and the dissociation energy of the R–H bond formed in reactions (27). By least squares, the following relationship was obtained

$$\lg\frac{k_{C_2H_6}}{k_{CH_4}} = -(0.048\pm0.005)D(R{-}H) + (6.62\pm0.50), \quad r = 0.913. \qquad (28)$$

As stated above (p. 222), the proportionality coefficient α of Polanyi's Eqn. (17) depends on the structure of the transition state for the reaction. If the ratio of the pre-exponential factors for the reactions with ethane and methane is independent (to a first approximation) of the nature of the attacking free radical, the dependence of α on $D(R-H)$ can easily be obtained from Eqn. (17). Thus, for the reactions with methane and ethane, we have

$$\alpha = \frac{E_{ac}^{CH_4} - E_{ac}^{C_2H_6}}{D(CH_3-H) - D(C_2H_5-H)}, \qquad (29)$$

$$\alpha = \frac{2.3RT}{6000}\lg\frac{k_{C_2H_6}}{k_{CH_4}} - \frac{2.3RT}{6000}\lg\frac{A_{C_2H_6}}{A_{CH_4}}, \qquad (30)$$

where $D(CH_3-H) = 104$ kcal mole^{-1}, $D(C_2H_5-H) = 98$ kcal mole^{-1}.[210] For $\lg(A_{C_2H_6}/A_{CH_4}) = \text{const} \simeq 0$, and $T = 373°K$, we have from Eqns. (28) and (30)

$$\alpha = \frac{2.3RT}{6000}[-(0.048\pm0.005)D(R{-}H) + (6.62\pm0.50)] =$$
$$= -(0.014\pm0.001)D(R{-}H) + (1.89\pm0.14) \qquad (31)$$

These ideas were tested by calculating α directly from formula (29), using published activation energies for the reactions of the radicals F$^{\cdot}$, Cl$^{\cdot}$, Br$^{\cdot}$, I$^{\cdot}$, ROO$^{\cdot}$, $CD_3^{\cdot}$, $CF_3^{\cdot}$, O$^{\cdot}$, H$^{\cdot}$, HO$^{\cdot}$. (The activation energies, as a rule, are known less accurately than the rate constants for the reactions. Hence, the values for the radicals $C_2F_5^{\cdot}$, n-$C_3F_7^{\cdot}$, and CN$^{\cdot}$, which were found to give an unsatisfactory correlation, were ignored). The result was

$$\alpha = -0.015D(R{-}H) + 2.03.$$

It is clear that the agreement with Eqn. (31) is excellent. The values $\alpha_{CH_3} = 0.44$ and $\alpha_{Br} = 0.66$ may be compared with those reported by Trotman-Dickenson (0.49 [127] and 0.86 [129] respectively).

Eqn. (31) is a quantitative statement of Hammond's postulate[10], since α varies from 0 to 1 on going from the initial to the final state[119]. Thus, in accordance with the postulate, the transition state for the most active radical (F$^{\cdot}$) is indistinguishable from the initial state, i.e. $\alpha = 0$,

Table 7. Kinetic parameters of the reactions of free radicals (R·) with methane, ethane, and propane, and dissociation energies of the bonds (D(R–H)).

Radical R·	k_{CH_4}	$k_{C_2H_6}$	$k_{C_3H_8}$	$\lg \frac{k_{C_2H_6}}{k_{CH_4}}$	$E_{CH_4} - E_{C_2H_6}$, kcal mole^{-1} [a]	α	D(R–H) kcal mole^{-1}
	cm^3 mole^{-1} s^{-1}						
CH_3·	$1.9 \cdot 10^8$ [180]	$7.0 \cdot 10^4$ [b, c 238, 239]	$8.0 \cdot 10^5$ [241]	1.57	3.15	0.44	104 [242]
CF_3·	$3.6 \cdot 10^5$ [b 198—200]	$17.6 \cdot 10^6$ [b 198, 243]	$7.6 \cdot 10^7$ [211]	1.69	2.0	0.40	106.3 [244]
C_2F_5·	$2.7 \cdot 10^5$ [245]	$12.2 \cdot 10^6$ [245]		1.655	1.9?	0.45	103 [244]
n-C_3F_7·	$2.7 \cdot 10^5$ [246]	$7.3 \cdot 10^6$ [246]		1.43	0.3?	0.45	103 [244]
H·	$1.38 \cdot 10^7$ [247]	$40.5 \cdot 10^7$ [248]	$2.1 \cdot 10^9$ [235]	1.47	2.6	0.43	104.2 [249]
HO·	$5.9 \cdot 10^{10}$ [250]	$10 \cdot 10^{11}$ [250]		1.23	1.4	0.22	119.2 [249]
ROO·	3.16 [251]	646 [251]	$3.7 \cdot 10^4$ [251]	2.31	4.0	0.63	90.0 [252]
O	$8.51 \cdot 10^7$ [253]	$4.85 \cdot 10^8$ [253]		1.755	3.1	0.46	102.3 [249]
F·	$1.9 \cdot 10^{13}$ [254]	$3.3 \cdot 10^{13}$ [254]	$1.1 \cdot 10^{13}$ [254]	0.24	0.93	0.0	135.5 [249]
Cl·	$4.0 \cdot 10^{11}$ [b 255, 256]	$24 \cdot 10^{12}$ [b 255, 256]	$29 \cdot 10^{12}$ [b 255, 256]	1.78	2.9	0.45	103.1 [249]
Br·	$1.4 \cdot 10^8$ [b 257—259]	$1.2 \cdot 10^6$ [b 258, 260]	$5.8 \cdot 10^7$ [258]	2.92	5.1	0.66	87.6 [249]
I·	$6.3 \cdot 10^{-6}$ [217]	$7.9 \cdot 10^{-3}$ [261]	0.43 [262]	3.11	6.2	0.89	71.3 [249]
CN	1	7.1 [d 263]	7.0 [d 263]	0.85	3.7?	0.34	111 [249]

a) Difference in activation energies; literature references are given in the previous columns. b) Mean value. c) Value of $k_{C_2H_6}$ calculated by using a corrected value of the rate constant for the reaction of the methyl radical with deuteroacetone [240]. d) Rate constants relative to the value for methane, taken as unity.

whereas for I· we have $\alpha = 0.89$, i.e. the transition state adopts the structure of the products almost completely. It follows that Eqns. (28) and (31) are correct only for the chosen range of D(R–H) values, since this range corresponds to a change of the transition state structure from the structure of the reactants to that of the products. In particular, when D(R–H) = 0, $\lg(k_{C_2H_6}/k_{CH_4}) \neq 6.62$ (the value required by Eqn. (28)).

In the reactions of $CH_3^{\cdot}$, $CF_3^{\cdot}$, Cl·, $C_2F_5^{\cdot}$, n-$C_3F_7^{\cdot}$, H·, and O· the transition state is "symmetrical" as expected, i.e. it is mid-way between the initial and the final configuration, since the dissociation energies of the bonds broken and formed in the reactions with methane are approximately equal for these radicals. Published data on the structure of the transition state for the reactions between methyl radicals and hydrocarbons support this conclusion (~50% of initial state character [185]), but earlier work [264] on the transition state of reactions with chlorine had detected only 10% of final state character in the transition state instead of 50% as found in our work. These results were obtained by comparing the differences in activation energy for the removal of primary and tertiary hydrogen atoms in triptane by chlorine atoms with the dissociation energies of these bonds.

However, the absolute rate constants for the reactions of chlorine with ethane, propane, and isobutane are approximately equal: $(2-3) \times 10^{13}$ cm^3 mole^{-1} s^{-1} at 100°. [255,256] Hence, the small difference in activation energy of these reactions is explained by the fact that practically every collision between the reactants leads to reaction—the upper limit of the rate constant for bimolecular reactions is given as 10^{14} cm^3 mole^{-1} s^{-1} by the collision theory—and changes in the structure of the alkane molecule have practically no effect on the reaction rate. However, on going from methane to ethane the rate of reaction of chlorine atoms increases approximately 60-fold (at 100°), and the activation energy changes by 2.9 kcal mole^{-1}, i.e. the reaction rate is very sensitive to the structure of the alkane. Hence, it is more correct to use these data to calculate the structure of the transition state.

It is interesting to note that the transition state has the same structure (~50% of initial state character) for a large number of radicals. This explains why the Polanyi–Semenov equation is so generally applicable.

From the above we may conclude that the increase in the rate constants of free-radical reactions on going from methane to ethane is due first of all to the decrease (by 6 kcal mole^{-1}) in the dissociation energy of the bond to be broken. Bond dissociation energies are also the rate determining factor in the reactions of other alkanes with free radicals. For each radical, the transition-state structure is the same in all the reactions, since Eqn. (17) applies. In the radical reactions of compounds whose substituents have strong polar and resonance effects (chloroform, toluene, etc.) the transition-state structure may differ from that of the same reactions with alkanes. Thus, the points for the reactions of the methyl radical with toluene and propylene [119] fall well away from the plot of Eqn. (17).

Eqns. (28) and (30) can be used either to calculate the kinetic parameters of free-radical reactions or to predict bond energy values (D(R–H)) and the parameter α. Thus, Pritchard and Perona [265] recently measured the rate constants of reactions (27) with the radical $CHF_2^{\cdot}$. They found $\lg(k_{C_2H_6}/k_{CH_4}) = 2.02$ at 100°. From Eqns. (28) and (31) we obtain $D(CHF_2\text{–H}) = 95.9$ kcal mole^{-1}, $\alpha = 0.55$. The experimental value of $D(CHF_2\text{–H})$ is 97.4 kcal mole^{-1}.

As was stated above (p. 226), the proportionality constant r^* of Eqn. (11) should depend on the structure of the transition state and therefore also on the parameter α. Unfortunately, the r^* values given in Table 5 refer to different temperatures, which makes it hard to compare them. However, there can be little doubt that r^* increases with α. (For example, $r^*_{I^{\cdot}} > r^*_{X(CH_2CH_2)^{\cdot}_n} > r^*_{CH_3^{\cdot}} = r^*_{CF_3^{\cdot}}$; the corresponding values of α from Eqn. (31) are 0.86, 0.52, 0.44, 0.40).

REFERENCES

1. L. P. Hammett, Chem. Rev., 17, 125 (1935).
2. R. W. Taft, Jnr., "Separation of Polar, Steric, and Resonance Effects in Reactivity", Chapter in "Steric Effects in Organic Chemistry" (Edited by M. S. Newman) (Translated into Russian), Inostr. Lit., Moscow, 1960.
3. H. C. Brown and Y. Okamoto, J. Amer. Chem. Soc., 79, 1913 (1957).
4. E. C. Kooyman, R. Helden, and A. F. Bickel, K. ned. Acad. Wetenschappen Proc., B56, 75 (1953).
5. R. Helden and E. C. Kooyman, Rec. Trav. chim., 73, 269 (1954).
6. C. Walling and B. Miller, J. Amer. Chem. Soc., 79, 4181 (1957).
7. G. A. Russell, J. Amer. Chem. Soc., 78, 1047 (1956).
8. C. Walling, E. R. Briggs, K. B. Wolfstirn, and F. R. Mayo, J. Amer. Chem. Soc., 70, 1537 (1948).
9. G. A. Russell, J. Org. Chem., 23, 1407 (1958).
10. G. S. Hammond, J. Amer. Chem. Soc., 77, 334 (1955).
11. E. Kalatzis and G. H. Williams, J. Chem. Soc., B, 1112 (1966).
12. W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, J. Org. Chem., 34, 2018 (1969).
13. E. S. Huyser, J. Amer. Chem. Soc., 82, 391 (1960).
14. R. F. Bridger and G. A. Russell, J. Amer. Chem. Soc., 85, 3754 (1963).
15. E. A. Trosman and Kh. S. Bagdasar'yan, Zhur. Fiz. Khim., 38, 2698 (1964) [Russ. J. Phys. Chem., No. 11 (1964)].
16. R. W. Taft, J. Phys. Chem., 64, 1805 (1960).
17. W. A. Prior, J. T. Echols, and K. Smith, J. Amer. Chem. Soc., 88, 1189 (1966).
18. E. I. Heiba, R. M. Dessau, and W. J. Koehl, J. Amer. Chem. Soc., 91, 138 (1969).
19. G. A. Russell and R. C. Williamson, J. Amer. Chem. Soc., 86, 2357 (1964).
20. J. Hradil and V. Chvalovsky, Coll. Czech. Chem. Comm., 33, 2029 (1968).
21. K. H. Lee, Tetrahedron, 25, 4357 (1969).
22. C. Walling, A. L. Rieger, and D. D. Tanner, J. Amer. Chem. Soc., 85, 3122 (1963).
23. C. Walling and A. L. Rieger, J. Amer. Chem. Soc., 85, 3135 (1963).
24. R. E. Pearson and J. C. Martin, J. Amer. Chem. Soc., 85, 3142 (1963).
25. C. Walling and B. B. Jacknow, J. Amer. Chem. Soc., 82, 6108 (1960).
26. R. D. Gilliom and B. F. Word, J. Amer. Chem. Soc., 87, 3944 (1965).
27. B. R. Kennedy and K. U. Ingold, Canad. J. Chem., 44, 2381 (1966).
28. R. D. Gilliom and J. R. Howley, Canad. J. Chem., 46, 2752 (1968).
29. H. Sakurai and A. Hosomi, J. Amer. Chem. Soc., 89, 458 (1967).
30. C. Walling and J. A. McGuiness, J. Amer. Chem. Soc., 91, 2053 (1969).
31. C. Walling and M. J. Gibian, J. Amer. Chem. Soc., 87, 3361 (1965).
32. V. D. Pokhodenko and V. A. Bidzina, Teor. Eksper. Khim., 2, 691 (1966).
33. R. S. Neale and E. Gross, J. Amer. Chem. Soc., 89, 6579 (1967).
34. E. P. Chang, R. L. Huang, and K. H. Lee, J. Chem. Soc., B, 878 (1969).
35. R. L. Huang and K. H. Lee, J. Chem. Soc., C, 935 (1966).
36. G. J. Gleicher, J. Org. Chem., 33, 332 (1968).
37. J. A. Howard, K. U. Ingold, and M. Symonds, Canad. J. Chem., 46, 1017 (1968).
38. W. D. Totherow and G. J. Gleicher, J. Amer. Chem. Soc., 91, 7150 (1969).
39. M. M. Martin and G. J. Gleicher, J. Org. Chem., 28, 3266 (1963).
40. T. P. Low and K. H. Lee, J. Chem. Soc., 535 (1970).
41. S. S. Friedrich, L. J. Andrews, and R. M. Keefer, J. Org. Chem., 35, 944 (1970).
42. S. S. Friedrich, E. C. Friedrich, L. J. Andrews, and R. M. Keefer, J. Org. Chem., 34, 900 (1969).
43. R. L. Huang and K. H. Lee, J. Chem. Soc., 5963 (1964).
44. R. L. Huang, K. H. Lee, and M. S. Malhotra, J. Chem. Soc., 5947 (1964).
45. R. L. Huang, H. H. Lee, and S. H. Ong, J. Chem. Soc., 3336 (1962).
46. K. H. Lee, Tetrahedron, 24, 4793 (1968).
47. K. H. Lee, Tetrahedron, 26, 1503 (1970).
48. K. H. Lee, Tetrahedron, 26, 2041 (1970).
49. L. Harvey, G. J. Gleicher, and W. D. Totherow, Tetrahedron, 25, 5019 (1969).
50. H. Sakurai, A. Hasomi, and M. Kumara, J. Org. Chem., 35, 993 (1970).
51. K. U. Ingold, Canad. J. Chem., 41, 2816 (1963).
52. M. A. Rooge and L. R. Manohey, J. Org. Chem., 32, 1 (1967).
53. J. C. McGowan, T. Powell, and R. Raw, J. Chem. Soc., 3103 (1959).
54. J. C. Hogg, D. H. Lohmann, and K. E. Russell, Canad. J. Chem., 39, 1588 (1961).
55. J. A. Howard and K. U. Ingold, Canad. J. Chem., 41, 1744 (1963).
56. M. Simonyi, F. Tudos, and J. Pospisil, Europ. Pol. J., 3, 101 (1967).
57. J. A. Howard and K. U. Ingold, Canad. J. Chem., 43, 2724 (1965).
58. Y. Schaafsma, A. F. Bickel, and E. C. Kooyman, Rec. Trav. chim., 76, 180 (1957).
59. S. C. Barton, R. A. Bird, and K. E. Russell, Canad. J. Chem., 41, 2737 (1963).
60. M. Simonyi and F. Tudos, Pre-prints of Papers, International Symposium on Macromolecular Chemistry, Budapest, 3, 119 (1969).
61. W. C. Danen and D. G. Saunders, J. Amer. Chem. Soc., 91, 5924 (1969).
62. A. Orochov and M. Asscher, J. Chem. Soc., B, 255 (1969).
63. T. Yamamoto and T. Otsu, J. Polymer Sci., B-4, 1039 (1966).
64. T. Yamamoto and T. Otsu, Kogyo Kagaku Zasschi, 70, 2403 (1967).
65. T. Yamamoto and T. Otsu, Chem. and Ind., 787 (1967).
66. T. Yamamoto and T. Otsu, J. Polymer Sci., A-1, 6, 49 (1968).
67. T. Yamamoto, S. Nakamura, M. Hasegawa, and T. Otsu, Kogyo Kagaku Zasschi, 72, 727 (1969).
68. T. Yamamoto, M. Hasegawa, and T. Otsu, Bull. Chem. Soc. Japan, 41, 2788 (1968).
69. T. Yamamoto, M. Hasegawa, and T. Otsu, Bull. Chem. Soc. Japan, 42, 1364 (1969).
70. T. Yamamoto and T. Otsu, J. Polymer Sci, A-1, 7, 1279 (1969).
71. R. Ito, T. Migita, N. Morikawa, and O. Simamura, Tetrahedron, 21, 955 (1965).
72. M. E. Kurz and M. Pellegrini, J. Org. Chem., 35, 990 (1970).
73. G. Martell, P. Spagnolo, and M. Tiecco, J. Chem. Soc., B, 1413 (1970).

74. P. Kovacic, C. G. Reid, and M. E. Kurz, J. Org. Chem., 34, 3302 (1969).
75. J. R. Shelton and C. W. Uzelmeier, J. Amer. Chem. Soc., 88, 5222 (1966).
76. M. M. Martin and G. J. Gleicher, J. Amer. Chem. Soc., 86, 233 (1964).
77. J. G. Cadogan and I. H. Sadler, J. Chem. Soc., B, 1191 (1966).
78. M. Imoto, K. Kinoshita, and N. Nishigaki, Makromol. Chem., 86, 217 (1965).
79. S. C. Dickerman, D. J. DeSouza, M. Fryd, I. S. Megna, and M. M. Skoultchi, J. Org. Chem., 34, 714 (1969).
80. M. Kobayashi, H. Minato, N. Watanabe, and N. Kobori, Bull. Chem. Soc. Japan, 43, 258 (1970).
81. M. Kobayashi, H. Minato, N. Kobori, and E. Yamada, Bull. Chem. Soc. Japan, 43, 1131 (1970).
82. B. Yamada, T. Hayashi, and T. Otsu, Kogyo Kagaku Zasschi, 71, 2045 (1968).
83. A. I. Prokof'ev, S. P. Solodovnikov, G. A. Nikiforov, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 558 (1970).
84. R. W. Taft, J. Amer. Chem. Soc., 75, 4231 (1953).
85. H. V. Hartel, N. Meer, and M. Polanyi, Z. phys. Chem., B19, 139 (1932).
86. I. B. Afanas'ev and A. A. Beer, Neftekhim., 2, 611 (1962).
87. F. W. Evans and M. Szwarc, Trans. Faraday Soc., 57, 1905 (1961).
88. I. B. Afanas'ev, T. N. Eremina, and E. D. Safronenko, Zhur. Org. Khim., 1, 844 (1965).
89. I. B. Afanas'ev, T. N. Eremina, S. A. Engovatova, and N. P. Leonova, Zhur. Org. Khim., 3, 237 (1967).
90. I. B. Afanas'ev and E. D. Safronenko, Zhur. Vses. Khim. Obshch. imeni Mendeleeva, 14, 462 (1969).
91. M. Anbar and E. J. Hart, J. Phys. Chem., 69, 271 (1965).
92. T. Migita, M. Kosugi, and Y. Nagai, Bull. Chem. Soc. Japan, 40, 920 (1967).
93. M. Kosugi, K. Takeuchi, and T. Migita, Bull. Chem. Soc. Japan, 42, 3242 (1969).
94. M. Kosugi, K. Takeuchi, and T. Migita, Bull. Chem. Soc. Japan, 42, 3354 (1969).
95. W. Mack, Tetrahedron Letters, 4993 (1967).
96. M. Kosugi, K. Takeuchi, and T. Migita, Bull. Chem. Soc. Japan, 43, 1535 (1970).
97. E. L. Patmore and R. J. Gritter, J. Org. Chem., 27, 4196 (1962).
98. Y. Nagai, K. Yamazaki, I. Shiojima, N. Kobori, and M. Hayashi, J. Organometal. Chem., 9, P21 (1967).
99. P. H. Owens, G. J. Gleicher, and L. M. Smith, J. Amer. Chem. Soc., 90, 4122 (1968).
100. G. J. Gleicher, J. L. Jackson, P. H. Owens, and J. D. Unruh, Tetrahedron Letters, 833 (1969).
101. M. M. Martin and G. J. Gleicher, J. Amer. Chem. Soc., 86, 242 (1964).
102. J. G. Kirkwood and F. H. Westheimer, J. Chem. Phys., 6, 503 (1938).
103. T. Otsu, T. Ito, T. Fukumizu, and M. Imoto, Bull. Chem. Soc. Japan, 39, 2257 (1966).
104. T. Otsu, T. Ito, and M. Imoto, J. Polymer Sci., B3, 113 (1965).
105. T. Otsu, K. Tsuda, and T. Fukumizu, Makromol. Chem., 119, 140 (1968).
106. K. Yokota, M. Kani, and Y. Ishii, J. Polymer Sci., A1, 6, 1325 (1968).
107. J. Wantier and A. Bruylant, Bull. Soc. Chim. Belg., 72, 222 (1963).
108. V. Ya. Katsobashvili, E. D. Safronenko, and I. B. Afanas'ev, Vysokomol. Soed., 7, 823 (1965).
109. V. Ya. Katsobashvili, E. D. Safronenko, and I. B. Afanas'ev, Vysokomol. Soed., 8, 282 (1966).
110. G. A. Gornowicz, J. W. Ryan, and J. L. Speier, J. Org. Chem., 33, 2918 (1968).
111. H. Sakurai, A. Hosomi, and M. Kumada, J. Org. Chem., 34, 1764 (1969).
112. K. Chikanishi and T. Tsuruta, Makromol. Chem., 73, 231 (1964).
113. T. Alfrey and C. C. Price, J. Polymer Sci., 2, 101 (1947).
114. C. H. Bamford, A. D. Jenkins, and R. Johnston, Trans. Faraday Soc., 55, 418 (1959).
115. C. H. Bamford and A. D. Jenkins, J. Polymer Sci., 53, 149 (1961).
116. C. H. Bamford and A. D. Jenkins, Trans. Faraday Soc., 59, 530 (1963).
117. C. Walling, "Free Radicals in Solution" (Translated into Russian), Inostr. Lit., Moscow, 1960.
118. C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, "Kinetics of Vinyl Polymerisation by Radical Mechanisms" (Translated into Russian), London, 1958.
119. Kh. S. Bagdasar'yan, "Teoriya Radikal'noi Polimerizatsii" (Theory of Radical Polymerisation), Izd. Nauka, Moscow, 1966.
120. B. A. Englin and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 2097 (1966).
121. B. A. Englin, B. N. Osipov, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 2223 (1967).
122. B. A. Englin, T. A. Onishchenko, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 2489 (1968).
123. B. A. Englin and B. N. Ospiov, Izv. Akad. Nauk SSSR, Ser. Khim., 2712 (1968).
124. N. Fuhrman and R. B. Mesrobian, J. Amer. Chem. Soc., 76, 3281 (1954).
125. M. Evans and M. Polanyi, Trans. Faraday Soc., 34, 11 (1938).
126. N. N. Semenov, "O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti" (Some Problems in Chemical Kinetics and Reactivity), Izd. Akad. Nauk SSSR, Moscow, 1958.
127. A. F. Trotman-Dickenson, Chem. and Ind., 379 (1965).
128. J. A. Kerr and D. Timlin, J. Chem. Soc., A, 1241 (1969).
129. A. F. Trotman-Dickenson, Adv. Free Radical Chem., 1, 1 (1965).
130. J. T. Herron and R. E. Huie, J. Phys. Chem., 73, 3327 (1969).
131. J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson, and J. C. Young, J. Chem. Soc., A, 510 (1968).
132. N. L. Arthur and P. Gray, Trans. Faraday Soc., 65, 434 (1969).
133. A. A. Zavitsas and S. Ehrenson, J. Amer. Chem. Soc., 87, 2841 (1965).
134. M. G. Evans, J. Gergely, and E. C. Seaman, J. Polymer Sci., 3, 866 (1948).
135. C. Walling, J. Phys. Chem., 64, 166 (1966).
136. R. P. Smith, T. Ree, J. L. Magee, and H. Eyring, J. Amer. Chem. Soc., 73, 2263 (1951).
137. R. S. Mulliken, J. Chim. Phys., 46, 497 (1949).
138. R. P. Smith and H. Eyring, J. Amer. Chem. Soc., 74, 229 (1952).
139. K. R. Wilson and D. R. Herschbach, Nature, 208, 182 (1965).
140. J. C. Polanyi, J. Chem. Phys. Letters, 1, 421 (1967).
141. J. Whittemore, A. P. Stefani, and M. Szwarc, J. Amer. Chem. Soc., 84, 3799 (1962).

142. A. P. Stefani, L. Herk, and M. Szwarc, J. Amer. Chem. Soc., 83, 4732 (1961).
143. A. P. Stefani, L.-Y. Y. Chuang, and H. E. Todd, J. Amer. Chem. Soc., 42, 4168 (1970).
144. C. A. Coulson, J. Chem. Soc., 1435 (1955).
145. K. Higasi, H. Baba, and A. Rembaum, "Quantum Organic Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1967.
146. M. Szwarc and D. Bink, Symposium "Theoretical Organic Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1963, p. 327.
147. A. P. Stefani and M. Szwarc, J. Amer. Chem. Soc., 84, 3661 (1962).
148. E. C. Kooyman, Tetrahedron, 19, Suppl. 2, 415 (1963).
149. K. R. Jennings and R. J. Cvetanovic, J. Chem. Phys., 34, 1233 (1961).
150. K. Yang, J. Phys. Chem., 67, 562 (1963).
151. J. E. Bloor, A. C. R. Brown, and D. G. L. James, J. Phys. Chem., 70, 2191 (1966).
152. I. E. Chlenov and M. V. Basilevskii, Zhur. Strukturnoi Khim., 8, 993 (1967).
153. J. D. Unruh and G. L. Gleicher, J. Amer. Chem. Soc., 91, 6211 (1969).
154. F. B. Moin, Uspekhi Khim., 36, 1223 (1967) [Russ. Chem. Rev., No. 7 (1967)].
155. Yu. G. Papulov, Zhur. Org. Khim., 37, 1191 (1967).
156. Z. G. Seabo, Symposium "Khimicheskaya Kinetika i Tsepnye Reaktsii" (Chemical Kinetics and Chain Reactions), Izd. Nauka, Moscow, 1966, p. 46.
157. T. Kagiya, Y. Sumida, T. Inoue, and F. S. Dyachkovski, Bull. Chem. Soc. Jap., 42, 1812 (1969).
158. T. Kagiya, Y. Sumida, and T. Inoue, Bull. Chem. Soc. Jap., 42, 2422 (1969).
159. E. D. Safronenko and I. B. Afanas'ev, Zhur. Org. Khim., 4, 2086 (1968).
160. E. D. Safronenko and I. B. Afanas'ev, Zhur. Org. Khim., 6, 209 (1970).
161. G. A. Mortimer, J. Polymer Sci., A1, 4, 881 (1966).
162. J. E. Hodgkins and E. D. Megarity, J. Amer. Chem. Soc., 87, 5322 (1965).
163. L. Gilbert and R. Kreilick, J. Chem. Phys., 48, 3376 (1968).
164. M. F. R. Mulcahy and D. J. Williams, Nature, 199, 761 (1963).
165. A. I. Prokof'ev, G. I. Nikiforov, S. P. Solodovnikov, and V. V. Ershov, Teor. Eksper. Khim., 3, 821 (1967).
166. S. P. Solodovnikov and A. I. Prokof'ev, Dokl. Akad. Nauk SSSR, 180, 158 (1968).
167. R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 39, 2147 (1963).
168. P. Smith, J. T. Pearson, P. B. Wood, and T. C. Smith, J. Chem. Phys., 43, 1535 (1965).
169. H. Fischer, Naturforsch., 19a, 866 (1964).
170. O. H. Griffith, J. Chem. Phys., 42, 2644 (1963).
171. G. A. Russell and J. Lokensgard, J. Amer. Chem. Soc., 89, 5059 (1967).
172. J. Bolton in "Radical Ions", E. T. Kaiser and L. Kevan (Editors), New York, 1968, p. 1.
173. O. H. Griffith, J. Chem. Phys., 42, 2651 (1963).
174. W. T. Dixon, Tetrahedron Letters, 2531 (1967).
175. I. B. Afanas'ev, Dokl. Akad. Nauk SSSR, 187, 1287 (1969).
176. I. B. Afanasev, Tetrahedron Letters, 1853 (1970).
177. I. B. Afanas'ev and E. D. Safronenko, Zhur. Org. Khim., 7, 453 (1971).
178. A. Carrington and J. C. P. Smith, Molecular Phys., 9, 137 (1965).
179. J. Lin, K. Tsuji, and F. Williams, Trans. Faraday Soc., 64, 2896 (1968).
180. F. S. Dainton, K. J. Ivin, and F. Wilkinson, Trans. Faraday Soc., 55, 929 (1959).
181. T. W. Shannon and A. G. Harrison, Canad. J. Chem., 41, 2455 (1963).
182. P. Gray and A. A. Herod, Trans. Faraday Soc., 64, 2723 (1968).
183. M. H. J. Wijnen, J. Chem. Phys., 28, 939 (1958).
184. M. H. J. Wijnen, J. Chem. Phys., 22, 1074 (1954).
185. A. F. Trotman-Dickenson, Quart. Rev., 7, 198 (1953).
186. A. Shepp, J. Chem. Phys., 24, 939 (1956).
187. J. C. J. Thynne and P. Gray, Trans. Faraday Soc., 58, 2403 (1962).
188. R. E. Rebbert and E. W. R. Steacie, J. Chem. Phys., 21, 1723 (1953).
189. L. F. Loucks, Canad. J. Chem., 45, 2775 (1967).
190. J. A. Kerr and J. G. Calvert, J. Phys. Chem., 69, 1022 (1965).
191. M. F. R. Mulcahy, B. G. Tucker, D. J. Williams, and J. R. Wilmshurst, Austral. J. Chem., 20, 1155 (1967).
192. R. J. Cvetanovic and R. S. Irwin, J. Chem. Phys., 46, 1694 (1967).
193. J. B. Burley and R. E. Rebbert, J. Chem. Phys., 67, 168 (1963).
194. M. F. R. Mulcahy, D. J. Williams, and J. R. Wilmshurst, Austral. J. Chem., 17, 1329 (1964).
195. M. Cher, C. S. Hollingsworth, and F. Silicio, J. Phys. Chem., 70, 877 (1966).
196. I. B. Afanas'ev, I. V. Mamontova, and G. I. Samokhvalov, Zhur. Org. Khim., 7, 457 (1971).
197. I. B. Afanas'ev and I. V. Mamontova, Zhur. Org. Khim., 7, 0000 (1971).
198. P. B. Ayscough, J. C. Polanyi, and E. W. R. Steacie, Canad. J. Chem., 43, 743 (1955).
199. H. Carmichael and H. S. Johnston, J. Chem. Phys., 41, 1975 (1964).
200. W. G. Alcock and E. Whittle, Trans. Faraday Soc., 61, 244 (1965).
201. W. G. Alcock and E. Whittle, Trans. Faraday Soc., 62, 134 (1966).
202. T. S. Carlton, J. R. Steeper, and R. L. Christensen, J. Phys. Chem., 70, 3222 (1966).
203. E. R. Morris and J. C. J. Thynne, Trans. Faraday Soc., 64, 414 (1968).
204. G. O. Pritchard and J. R. Decay, Canad. J. Chem., 38, 182 (1960).
205. N. L. Arthur, P. Gray, and A. A. Herod, Canad. J. Chem., 47, 1347 (1969).
206. R. E. Dodd and J. W. Smith, J. Chem. Soc., 1465 (1957).
207. J. L. Holmes and K. O. Kutschke, Trans. Faraday Soc., 58, 333 (1962).
208. M. V. Bazilevskii and N. I. Piskun, Zhur. Fiz. Khim., 39, 951 (1965) [Russ. J. Phys. Chem., No. 4 (1965)].
209. M. V. Bazilevskii and Kh. S. Bagdasar'yan, Kinetika i Kataliz, 5, 215 (1964).
210. M. V. Bazilevskii and N. I. Piskun, Zhur. Fiz. Khim., 39, 762 (1965) [Russ. J. Phys. Chem., No. 3 (1965)].
211. B. Chutny, Coll. Czech. Chem. Comm., 31, 358 (1966).
212. J. K. Thomas, Trans. Faraday Soc., 61, 702 (1965).
213. J. H. Baxendale et al. (Editors), "Pulse Radiolysis", London and New York, 1965, p. 131.
214. M. Anbar, D. Meyerstein, and P. Neta, J. Chem. Soc., B, 742 (1966).

215. G. Scholes and R. L. Willson, Trans. Faraday Soc., 63, 2983 (1967).
216. J. H. Merz and W. A. Waters, J. Chem. soc., S 15 (1949).
217. D. M. Golden, R. Walsh, and S. W. Benson, J. Amer. Chem. Soc., 87, 4053 (1965).
218. D. M. Golden and S. W. Benson, Chem. Rev., 69, 125 (1969).
219. D. M. Golden, A. S. Rodgers, and S. W. Benson, J. Amer. Chem. Soc., 88, 3196 (1966).
220. R. Walsh, D. M. Golden, and S. W. Benson, J. Amer. Chem. Soc., 88, 650 (1966).
221. J. T. Clarke, R. O. Howard, and W. H. Stockmayer, Makromol. Chem., 44-46, 427 (1961).
222. S. R. Palit and S. K. Das, Proc. Roy. Soc., A226, 82 (1954).
223. R. D. Spencer, M. B. Fulton, and B. H. Beggs, Amer. Chem. Soc., Div. Polymer Chem. Preprint, 1, 126 (1960).
224. A. Vansheidt and G. Hardy, Acta Chim. Acad. Sci. Hung., 20, 261, 381 (1959).
225. M. Matsumoto, J. Ukida, G. Takayama, T. Eguchi, K. Mukumoto, K. Imai, Y. Kazusa, and M. Maeda, Makromol. Chem., 32, 13 (1959).
226. S. F. Thompson, W. S. Port, and L. P. Witnauer, J. Amer. Chem. Soc., 81, 2552 (1959).
227. F. A. Raal and E. W. R. Steacie, J. Chem. Phys., 20, 578 (1952).
228. S. H. Ridge and E. W. R. Steacie, Canad. J. Chem., 33, 396 (1955).
229. R. O. King and E. S. Swinboure, J. Phys. Chem., 71, 237 (1967).
230. A. Hudson and K. O. J. Root, J. Chem. Soc., B, 656 (1970).
231. G. Hughes and H. A. Makada, Trans. Faraday Soc., 64, 3276 (1968).
232. B. G. Gowenlock and K. E. Thomas, J. Chem. Soc., 5068 (1965).
233. Y. Nagai, M. Kosugi, K. Takeuchi, and T. Migita, Tetrahedron, 26, 3791 (1970).
234. S. W. Benson, J. Amer. Chem. Soc., 80, 5151 (1958).
235. H. A. Kazmi and D. J. LeRoy, Canad. J. Chem., 42, 1145 (1964); D. M. Bishop and K. J. Laidler, J. Chem. Phys., 42, 1688 (1965).
236. S. W. Benson, "The Foundations of Chemical Kinetics" (Translated into Russian), Izd. Mir, Moscow, 1964.
237. I. B. Afanas'ev, Kinetika i Kataliz, 12, No. 2 (1971).
238. M. H. J. Wijnen, J. Chem. Phys., 23, 1357 (1955).
139. J. R. Nesby and A. S. Gordon, J. Amer. Chem. Soc., 77, 4719 (1955).
240. P. Gray and A. A. Herod, Trans. Faraday Soc., 64, 1568 (1968).
241. W. M. Jackson, J. R. McNesby, and B. B. Darwent, J. Chem. Phys., 37, 1610 (1962).
242. J. A. Kerr, Chem. Rev., 66, 465 (1966).
243. P. B. Ayscough and E. W. R. Steacie, Canad. J. Chem., 34, 103 (1956).
244. J. W. Coomber and E. Whittle, Trans. Faraday Soc., 63, 2656 (1967).
245. G. O. Pritchard, J. R. Dacey, W. C. Kent, and C. R. Simonds, Canad. J. Chem., 44, 171 (1966).
246. G. Giacometti and E. W. R. Steacie, Canad. J. Chem., 36, 1493 (1958).
247. R. W. Walker, J. Chem. Soc., **A**, 2391 (1968).
248. V. V. Azatyan and S. B. Filippov, Dokl. Akad. Nauk SSSR, 184, 625 (1969).
249. V. I. Vedeneev et al., "Energiya Razryva Khimicheskikh Svyazei" (Dissociation Energy of Chemical Bonds), Izd. Akad. Nauk SSSR, Moscow, 1962.
250. D. G. Horne and R. G. W. Norrish, Nature, 1373 (1967).
251. S. W. Benson, J. Amer. Chem. Soc., 87, 972 (1965).
252. J. Heicklen, Adv. Chem. Ser., 76, 23 (1968).
253. A. A. Westenberg and N. de Haas, J. Chem. Phys., 50, 2512 (1969).
254. G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, J. Chem. Soc., 1064 (1960).
255. J. H. Knox and R. L. Nelson, Trans. Faraday Soc., 55, 937 (1959).
256. R. Eckling, P. Goldfinger, G. Huybrechts, G. Martens, L. Meyers, and S. Smoes, Ber., 93, 3014 (1960).
257. G. B. Kistiakowsky and E. R. Van Artsdalen, J. Chem. Phys., 12, 469 (1944).
258. G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, J. Chem. Soc., 4177 (1960).
259. A. M. Tarr, J. W. Coomber, and E. Whittle, Trans. Faraday Soc., 61, 1182 (1965).
260. J. W. Coomber and E. Whittle, Trans. Faraday Soc., 62, 1553 (1966).
261. D. B. Hartley and S. W. Benson, J. Chem. Phys., 39, 132 (1963).
262. P. S. Nandia and S. W. Benson, J. Amer. Chem. Soc., 86, 2773 (1964).
263. C. A. Goy, D. H. Shaw, and H. O. Pritchard, J. Phys. Chem., 69, 1504 (1965).
264. G. A. Russell and H. C. Brown, J. Amer. Chem. Soc., 77, 4031 (1955).
265. G. O. Pritchard and M. J. Perona, Internat. J. Chem. Kinetics, 1, 509 (1969).

All-Union Research Institute for
Vitamins, Moscow