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Reactivity of Radicals and Molecules in Radical Reactions

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A survey is made of the effect of polar interactions, due to substituents and the medium, on the reactivity of radicals and molecules in radical additions (polymerisation of monomers), and the metathesis and decomposition of molecules. Analysis of experimental information by the perturbation method leads to the conclusion that the reactivity of radicals increases, while that of molecules falls, with increase in their electronegative properties produced by the introduction of substituents, interaction with the solvent, etc. The non-additivity of the polar effect of substituents, which is known from the copolymerisation of vinyl monomers, is apparent also in several other reactions. A list of 94 references is included.

I. INTRODUCTION

If only physical constants are used, the description of a reacting system by the equations of quantum physics cannot give solutions which are suitable for practical application to complicated systems. This led to the need to introduce parameters of the hypothetical constants for a given configuration of atoms and electrons, such as the Coulombic and exchange integrals. As the result of the work of London[1] and of Eyring[2] this way of stating the problem for radical reactions enabled the valence bond method to be used to decipher the nature of the activation barrier in chemical reactions and to estimate the rate constant of the exchange between a hydrogen atom and a hydrogen molecule. A significant consequence of this work for an understanding of any radical reaction was the possibility of regarding activation energy as the superposition of bonding and antibonding terms. Analysis of radical reactions from this point of view permitted the extremely important Polanyi–Semenov rule to be formulated[3], which enabled the activation energy of a radical reaction to be estimated from the properties of the reactants. Comparison of this rule with experimental results showed that it had several significant exceptions[3]. Several of them can be described by regarding the rule as a consequence of the London relation and introducing the polarisability as an additional parameter[4]. The need to consider polarisability indicates that the higher unoccupied orbitals of the reactants have a considerable effect on the activation energy. However, no soundly based analysis of the dependence of activation energy on the properties of the reactants has been undertaken by the valence bond method, apparently owing to the difficulties of allowing for the large number of structures necessary for calculating the energy of a complicated polyatomic system of variable configuration.

The molecular orbital (MO) method provides considerably greater opportunities for ascertaining the dependence of reactivity on the structure of the reactants. With atomic orbitals as basis, however, the molecular orbital method does not enable the concept of activation barrier to be formulated, because incorrect allowance is made for the antibonding terms. In the analysis of radical reactions by the molecular orbital method[5-7], therefore, it is postulated that the activation energy E is related to some parameter Z of the system, which can be calculated by the molecular orbital method, using the relation

$$E = C + \alpha Z \qquad (1)$$

where C is constant for a given series of reactions of the same type, and α is a coefficient of proportionality.

The energies of localisation, stabilisation, hyperconjugation, etc. have been used as Z. A feature of the Z parameters is that by means of them the effect of a substituent as a whole is described, without separating it into components, e.g. into polar and resonance interactions. A satisfactory description of experimental results can usually be obtained, this being achieved in several cases by a "happy choice" either of the characteristics of the atoms or of the parameter Z.

The relation (1) can be satisfied if bonding and antibonding terms are connected by a linear dependence, which cannot be correct in general, since during the reaction these terms depend on different variables. Such proportionality is apparently observed in some reactions of a given type. Thus the relation (1) is observed in the polymerisation of vinyl hydrocarbons and in the abstraction of a hydrogen atom from hydrocarbons, whereas departures from this relation are found in the polymerisation of vinyl compounds containing heteroatoms[5,6,8].

Bazilevskii[8] has recently been able to overcome certain difficulties and show that the effect of the antibonding terms can be allowed for in the molecular orbital method. An activation barrier arises, in molecular orbital calculations on a reaction, if we pass by some method from a non-orthogonal set of atomic orbitals to an orthogonal set, i.e. if we make more correct allowance for repulsion between the reactants. In this case an expression is obtained for the energy of a system having non-zero activation energy in Pople's approximation. By using generally accepted assumptions this author[8] has calculated the activation energy for the reaction of the methyl radical with ethylene and has also described the effect of substituents on the activation energies of the polymerisation of several vinyl compounds.

In spite of the attractiveness of semi-empirical methods for calculating the activation energies and the rate constants of chemical reactions, their application to actual systems is at present essentially illustrative in character, since the large number of approximations in the values of atomic and bond parameters, both in the initial and especially in the transition states, leads in several cases to indeterminate results and divergence from experiment. As a consequence the advantages of the method, consisting in the possibility of calculating the effect of differential changes in the structure and the composition of the reactants on the rate of the reactions, have not yet been effectively realised. A considerable amount of work is evidently still necessary on evaluating atomic and bond parameters and elucidating the form of dependence of reactivity on these parameters before it will become possible to investigate reactions by a method of calculation.

An empirical method of investigating reactions, which has been termed the principle of the linear dependence of free energy of activation on structural parameters[9,10], has acquired great practical value. It is based on the hypothesis that the influence of fragments of molecules and radicals (ions) which remain unchanged during the reactions, i.e. substituents at the reaction centre, can be divided into three independent types of interaction—steric, polar (inductive), and resonance—and that the effectiveness of a substituent in the corresponding interaction can be determined by one parameter. Because of the impossibility of an unambiguous separation of the forms of interaction, these parameters have no physically based units of measurement, and are determined as relative values from reactions chosen as a standard. Only polar interactions could in practice be described with satisfactory accuracy, and scales of polar (inductive) constants compared for the substituents. The existing Hammett, Taft, etc. constants[9] differ mainly in the way in which allowance is made for the effect of conjugation. It is possible also to set up scales for the effectiveness of substituents for conjugation (resonance) with the reaction centre. Thus the Q scale is known for describing the ability of vinyl monomers to undergo copolymerisation[11]. Steric interactions cannot be described by a single scale.

Mathematically this principle is equivalent to expanding the free energy of activation $\Delta F^{\neq}$ in a series involving the parameters X_i describing the properties of the structure:

$$\Delta F^{\neq} = \Delta F_0^{\neq} + \frac{\partial \Delta F^{\neq}}{\partial X_i} dX_i + \frac{\partial^2 \Delta F^{\neq}}{\partial X_i^2} dX_i^2 + \dots \qquad (2)$$

and to the assumption that the first approximation, i.e. retention of terms in the first derivatives, is sufficient to describe the experimental results. Since the free energy of activation depends both on the entropy and on the energy of activation, which in general are not interrelated, and all types of interaction are involved in the reaction, the successful description of a series of reactions using only one variable as its first derivative, must be regarded as the exception rather than the rule. Actually, a so called "compensation effect" is evident in many cases, represented by a linear dependence of the variation in energy and entropy of activation, conjugation and polarity, etc. There are reactions for which taking only the first approximation (additive action of substituents) into account is insufficient. The well studied radical copolymerisation of vinyl monomers is described only by allowing for the non-additive polar interaction of the substituents (the Alfrey–Price relation[5,11]), which corresponds formally to the second approximation (2). In view of the fact that non-additivity of the substituent effects may appear in other reactions, and of the arbitrary character of the separation of the overall effect of substituents into polar and resonance components, it is more correct to regard the influence of substituents as a small perturbation of the reaction centre, which enables non-linear terms in the expansion to be used for the analysis. A new possibility then appears for describing the influence of the structure of the reactants on their reactivity, by calculating the characteristics of the substituents and the constants for series of reactions by semi-empirical methods.

The laws of radical reactions have been more fully studied than those of other reactions, because they vary little with the external conditions. The effect of conjugation on the reactivity of radicals and molecules has been well investigated, and quite satisfactory criteria have been obtained in both the semi-empirical method (stabilisation, localisation, etc. energies) and in the empirical method (heat of reaction)[5-7]. Steric interactions have no common quantitative criteria, which makes their analysis difficult. The σ_S-parameters, introduced by Taft[9], are suitable only for a relatively narrow range of reactions. Information on the effect of steric interactions in homolytic reactions is in most cases qualitative in character and does not allow of generalisation[12]. It may be regarded as fortunate that the steric effect always promotes a decrease in interaction between the reactants, i.e. a decrease in the rate of bimolecular reactions and an increase in unimolecular reactions, so that its role can always be determined qualitatively.

Hardly any general analysis has been made of the effect of polar interactions, in spite of a large number of investigations and also particular relations concerned mainly with the effect of substituents on the activity of molecules. The display of polar interactions in radical reactions and elucidation of the common features thereof constitute the subject of the present Review. Consideration is given to the polar effect of substituents and of the medium on bimolecular substitutions and additions (polymerisation) and the formation of radicals.

II. POLAR EFFECTS OF SUBSTITUENTS IN ADDITION AND SUBSTITUTION

Data on reaction series of radical substitutions and additions are assembled in Table 1. In most of the systems investigated aromatic compounds have been chosen[9] as reactant molecule, the choice of scale (σ) leading to no great differences in the ρ-values for these compounds, as can be judged, for example, from the reaction series 21–25, for which σ and σ^+ scales have been used. This permits a comparative analysis in qualitative form, without the necessity for laborious recalculation. For the additions 13, 14, 46, and 47 the properties of the substituents are characterised by the Taft σ^*-constants. It may be supposed that, since in this case the substituents are separated from the reaction centre by a C=O group, the transfer coefficient of the polar effect through which apparently differs little from the transfer coefficient through a CH_2 group ($\frac{1}{3}$), the range of ρ-values for these reactions is closed to the remaining reactions.

Most reaction series are satisfactorily described by using only one parameter (σ). Only in certain reaction series, e.g. 12, 17, 48, are deviations found, which were explained by conjugation of the substituents with the reaction centre, not taken into account by σ.

It may be noted from Table 1 that the "sensitivity" ρ of the reaction centre is in most reactions negative: i.e. electron-donor substituents in a molecule increase the reaction velocity, whereas electron-acceptor substituents slow down the reaction. The relation of a radical to a molecule in these reactions resembles that of an acid to a base, the role of acid being played by the radical, and that of the base by the molecule. Only for a relatively small number of reactions is $\rho \geqslant 0$: for the addition of benzyl, phenyl, and poly(methyl acrylate) radicals to a double bond (series 12–14, 46–48, 54–56) and for the abstraction of a hydrogen atom by methyl (11) and benzyl (17) radicals. The negative sign of ρ is explained by most authors[5,13,22] by the electron-acceptor properties of the radicals. Indeed, Table 1 shows a tendency for ρ to decrease with increase in the acceptor properties of the radicals. Thus on passing from the benzyl (17, 48) to the methyl (11) and then to the trichloromethyl radical the value of ρ diminishes from +0.8 to −1.75 (26, 45). An analogous tendency is observed with phenylated radicals (52–56). The value of ρ is also

Table 1. Reaction series of radical reactions.

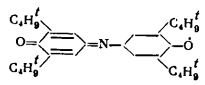
Series No.	Radical	Molecule*	Reaction conditions (t °C, solvent)	Constants: substituent	Constants: reaction series	Ref.
1	$\dot{Br}$	$\overset{\times}{C}H_3$—PhX	80; CCl_4	σ^+	−1.38	13
2	ditto	CH_3—$\overset{\times}{C}H_2$—PhX	ditto	ditto	−0.69	13
3	»	CH_2=CH—$\overset{\times}{C}H_2$—PhX	69.5; chlorobenzene	»	−0.76	13
4	»	(CH_3O_2)—$\overset{\times}{C}H$—PhX	80; CCl_4	»	−0.38	13
5	»	CH_3O—$\overset{\times}{C}H_2$—PhX	ditto	»	−0.35	13
6	»	$PhCH_2O\overset{\times}{C}H_2PhX$	»	»	−0.12	13
7	»	$CH_3O\overset{\times}{C}H$ (PhX) Ph	»	»	0	13
8	$\dot{RO}_2$ **	$(CH_3)_2\overset{\times}{C}HPhX$	90	σ	−0.4	14
9	ditto	$\overset{\times}{C}H_3PhX$	ditto	ditto	−0.6	14
10	$(CH_3)_3C\dot{O}$	ditto	110; γ-picoline	»	−0.5	15
11	$C\dot{H}_3$	»			0	16
12	R (Ph) $C\dot{H}$	$CH_2^{\times}$ = CHPhX	30	σ	0.6	17
13	ditto	$CH_2^{\times}$ = CHCOOX	60	σ*	0.56	18
14	»	$CH_2^{\times}$ = C (CH_3) COOX	ditto:	ditto	0.3	19
15	$\dot{C}Cl_3$	PhCH = CHPhX	105	σ^+	−0.7	20
16	$\dot{S}CH_2COOR$	ditto	ditto	ditto	−0.4	20
17	R (Ph) $C\dot{H}$	$(CH_3)_2\overset{\times}{C}HPhX$	60	σ	0.7	21
18	$R\dot{O}_2$	$\overset{\times}{H}OPhX$	65, styrene	σ^+	−1.49	22
19	ditto	$\overset{\times}{H}O$ (2,6- -t- C_4H_9) PhX	140; 160; oil	σ	−1.01	22
20	»	HOPhX	62.5; chlorobenzene	ditto	−3.7	22
21	»	»	44.4; methyl methacrylate	»	−3.48	22
				σ^+	−2.28	22
22	DPPH***	»	30; benzene	σ^+	−3.22	22
					−2.77	22
23	DPPH***	$\overset{\times}{H}OPhX$	20; CCl_4	σ	−6.4	22
				σ^+	−4.54	22
24	$\dot{R}$	HSPhX	110; toluene	σ	−0.433	22
				σ^+	−0.287	22
25	$R\dot{O}_2$	$(CH_3)_2\overset{\times}{C}HPhX$	60; chlorobenzene	σ	−0.54	22
				σ^+	−0.375	22
26	$\dot{C}Cl_3$	$\overset{\times}{C}H_3PhX$	50; chlorobenzene	σ^+	−1.46	22
27	$\dot{Br}$	ditto	80; chlorobenzene	»	−1.39	22
28	ditto	»	29; chlorobenzene	»	−1.78	22
29	$\dot{Cl}$	»	40; benzene, CCl_4	σ	−0.76	22
				σ^+	−0.66	22
30	$(CH_3)_3C\dot{O}$	»	110; γ-picoline	σ	−0.741	22
				σ^+	−0.646	22
31	ditto	»	40; reactants	σ	−0.821	22
				σ^+	−0.695	22
32	$PhCO\dot{O}$	$PhCH_2O\overset{\times}{C}H_2PhX$	80; reactants	σ	−0.957	22
				σ^+	−0.647	22
33	Indophenoxyl****	$\overset{\times}{H}_2NPhX$	30; xylene	σ	−2.53	23
34	»	$\overset{\times}{H}OPhX$			~0	24
35	»	$\overset{\times}{H}O$ — (2,6 -t- -C_4H_9) PhX		σ^+	>0	24
36	$(CH_3)_3C\dot{O}$	$\overset{\times}{H}OPhX$	122; CCl_4	σ^+	−1.19	25
37	»	ditto	122; chlorobenzene	»	−0.74	25
38	»	$\overset{\times}{H}O$ (2,6- -t- -C_4H_9)PhX	122; CCl_4	»	−0.86	25
39	»	ditto	122; chlorobenzene	»	−0.78	25
40	$\dot{Ph}$	$\overset{\times}{C}H_3PhX$		σ^0	−0.5	5
41	$R\dot{O}_2$	ditto		»	−0.77	5
42	Cl	»		»	−0.86	5
43	$\dot{Br}$	»		»	−0.97	5
44	Succinimido*****	»		»	−1.55	5
45	$\dot{C}Cl_3$	»		»	−1.75	5
46	R ($Ph\dot{C}H$)	$CH_2^{\times}$ = C (CH_3) COX		σ*	0.33	26
47	R ($ClCH_2CH_2OCO$)·$\dot{C}CH_3$	ditto		»	0.13	26
48	R (p-CH_3Ph) $C\dot{H}$	$C\dot{H}$ (CH_3) PhX		σ	0.8	27
49	$\dot{O}H$	$\dot{P}hX$		σ	−0.41	28
50	»	$\dot{O}COPhX$		ditto	−0.41	28
51	$\dot{H}$	$\dot{P}hX$		»	−0.7	29
52	p-$NO_2\dot{P}h$	$\dot{P}hX$	20; benzene	»	−0.7	29
53	p-$Cl\dot{P}h$	ditto	ditto	»	−0.27	30
54	$\dot{P}h$	»	»	»	0.05	30
55	p-$CH_3\dot{P}h$	»	»	»	0.08	30
56	p-$CH_3O\dot{P}h$	»	»	»	0.09	30

*The sign × indicates the site of the reaction.

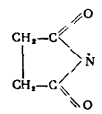
**R is an alkyl radical or a radical linked to the reaction centre by a CH_2 group.

***The diphenylpicrylhydrazyl radical.

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less than zero for electronegative radicals (Br•, Cl•, RO•, RO_2•, R_2N•). The minimum value of ρ is observed with the diphenylpicrylhydrazyl radical, which is apparently explained by the electron-acceptor properties of nitro-groups.

The effect of the structure of the molecule on the value of ρ is less clearly developed. On examining the reaction series 1 and 2, 8 and 9, 13 and 14 we can see that replacing hydrogen by a methyl group in the molecule leads to a decrease in the modulus ρ. For phenols and aromatic amines (18–23, 24, 33–38) the value of ρ is in most cases negative, and for vinyl compounds it is indeterminate (12–16, 46, 47). The magnitude of ρ apparently increases as the electron-donor power of the molecule becomes stronger, but this tendency is very weak.

To analyse the dependence of reactivity on the structure of the reactants, let us expand the reaction rate constant in a series:

$$\lg k_{ij} = \lg k_0 + \left(\frac{\partial \lg k}{\partial \sigma}\right)_R \sigma_i + \left(\frac{\partial \lg k}{\partial \sigma}\right)_M \sigma_j + \left[\left(\frac{\partial}{\partial \sigma}\right)_R \sigma_i + \left(\frac{\partial}{\partial \sigma}\right)_M \sigma_j\right]^2 \lg k + \ldots \quad (3)$$

where k_0 is the reaction rate constant disregarding polar interactions, and σ a measure of the polar properties of the substituents in the radical R and the molecule M, e.g. the Hammett, Taft, Alfrey–Price, etc. constants. Since the Alfrey–Price relation, including terms in $\sigma_i\sigma_j$, is observed in radical copolymerisations, whereas a linear dependence on σ is found with most reactions, it is apparent that in general it is sufficient to confine ourselves to the approximation

$$\lg k_{ij} = \lg k_0 + \rho_R\sigma_i + \rho_M\sigma_j + \rho_{RM}\sigma_i\sigma_j \quad (4)$$

for the rate constant, in which terms in σ_i^2 and σ_j^2 are neglected in comparison with Eqn. (3), in view of their smallness or indistinguishability from terms in σ, while the constants ρ denote the corresponding derivatives with respect to σ.

Experimentally reaction series are usually investigated, in which the relative rate of addition of a molecule containing different substituents to some radical is determined: i.e. the σ_i are constant for a series, and presumably also k_0, this converts formula (4) into

$$\lg \frac{k_{ij}}{k_0} = (\rho_M + \rho_{RM}\sigma_i)\sigma_j \equiv \rho_{exp}\sigma_j \qquad (5)$$

which is formally analogous to the Hammett, Taft, etc. relations. Equation (5) shows that the experimental quantity ρ_{exp} gives no information on the "sensitivity" of the radical to the polar effect of its substituents, since the term in ρ_R is constant in a given series of reactions, and is included in $k_0' = k_0 + \rho_R\sigma_i$. The sign and magnitude of ρ_{exp} give information only on the energy of polar interaction of substituents in the molecule with the radical or its substituents and on the "sensitivity" of the molecule. As already remarked, the magnitude of ρ_{exp} diminishes with increase in the electronegativity of the radical, which can be related to the quantity σ_i. Hence $\rho_{RM} < 0$. If we examine reaction series for different hydrocarbon radicals towards a single series of molecules for which ρ_M is constant, the whole difference in ρ_{exp} is determined by the electronegativity of the substituents in the radical, not by the properties of the radical as such. This is an important confirmation of the correctness of the Alfrey–Price relation in reactions involving detachment of a hydrogen atom. The negative sign of ρ_{RM} is explained by the effect of polar structures on the energy of the transition state in radical reactions, from which it follows that differently charged substituents in radical and monomer lower the energy of the transition state[5].

Existing data do not enable the sign of ρ_M to be assessed. Since for most reactions $\rho_{exp} < 0$ and $\rho_{RM} < 0$, it can be assumed that ρ_M is small and apparently slightly exceeds zero.

To determine ρ_R data are required on the absolute or relative rate constants in the reactions of different radicals with some one molecule. The experimental difficulties in the way of carrying out such a programme are great, which explains the extraordinary sparsity of such data. Bagdasar'yan's monograph[5] gives data on the absolute constants for addition of the radicals $CH_3^\bullet$, $CCl_3^\bullet$, and $CF_3^\bullet$ to hept-1-ene at 60°C, which are respectively 0.0005, 0.00062, and 1.7 $M^{-1}\,s^{-1}$, and which indicate an increase in reactivity of the radicals with increase in the electronegativity of the substituents, this occurring in spite of an increase in the energy of conjugation in the radical on the introduction of substituents. Some conformation of the increase in activity of the radicals with increase in electronegativity is the decrease in activation energy in the detachment of hydrogen from alkanes on passing from the radical $CH_3^\bullet$ to $CF_3^\bullet$.[4] The literature contains hardly any systematic data on the absolute rate constants for reactions involving the detachment of hydrogen. In this connection great significance is acquired by results obtained for the polymerisation and copolymerisation of vinyl monomers, from which reliable values of the relative reactivity of monomers have now been obtained. There are considerably fewer data on the relative reactivity of radicals and on the absolute rate constants, and they are less reliable. Existing data on the absolute rate constants of chain growth can, on certain assumptions concerning the energy of conjugation in the monomers, be described by means of Eqn. (4). With $\rho_{RM} = -1$† it was found[31,32] that $\rho_R = 1.6$ and $\rho_M = -0.35$: i.e. in polymerisation reactions the radical is more "sensitive" than the monomer to the polar effect of substituents, and further the effects of substituents in the radical and in the monomer are opposite in sign. From the fact that $\rho_R > 0$ it follows that electron-acceptor substituents increase the reactivity of radicals, whereas electron-donor substituents diminish it. Indirect data indicate that such a relation cannot be a particular case, but it is characteristic of all radical reactions involving molecules containing substituents at the site of formation of the radical. This generalisation is not valid for the addition of radicals to $\alpha\beta$-substituted vinyl compounds, owing to the change in nature of the interaction of the substituents: i.e. formula (4) is not applicable to such reactions. Thus in the copolymerisation of β-fluorinated styrenes (2), in which the fluorine has relatively little influence on the steric interactions, with styrene itself (1) it is found[35] that $r_1 = K_{11}/K_{12} > 1$, while $r_2 = K_{22}/K_{21} \to 0$, i.e. $K_{22} \to 0$. Formal treatment of these results on the basis of the Q–e (or Q'–e) scheme[31,32] for β-fluorostyrenes yields $e_2 > e_1$ and $Q_2 \to 0$. The latter is, of course, incorrect, since the energy of conjugation in β-fluorostyrenes is close to that in styrene itself, and $Q_2 \simeq 1$. A correct description of such systems needs to take into account terms in the expansion of the expression for the rate constants describing the effect of β-substituents.

Summarising, we can conclude that the introduction of electron-acceptor substituents into a radical, or increasing the electronegativity of the radical, increases its "sensitivity" to polar changes in the molecule, and increases the reactivity of the radical. Electron-acceptor substituents in the molecule (at the site of formation of the radical) change reactivity mainly by polar interaction with the radical or with substituents therein.

III. EFFECT OF THE POLAR PROPERTIES OF SUBSTITUENTS ON THE DECOMPOSITION OF PEROXIDES AND AZO-COMPOUNDS

The influence of the polarity of substituents on the rate constants for decomposition of organic compounds involving the formation of two radicals has been investigated mainly with peroxides and azo-compounds as examples.

The decomposition of substituted benzoyl peroxides was described by Swain and his coworkers[36], who discovered the additive effect of substituents, present in the rings of different aromatic peroxides, on the reaction rate constant:

$$\lg \frac{k}{k_0} = -0.38(\sigma_1 + \sigma_2).$$

These workers also concluded that the term in $\sigma_1\sigma_2$, describing the interaction of the substituents, was small or even absent.

Later investigations[37] have led to the conclusion that the effect of substituents on the decomposition of substituted benzoyl peroxides is described by a more complicated relation, and that conjugation of the reaction centre with a substituent exerts a considerable influence on the decomposition rate constant. Table 2 lists data obtained by different workers[36–38] on the decomposition of peroxides. It shows that electron-donor substituents accelerate decomposition, whereas electron-acceptor substituents slow de-

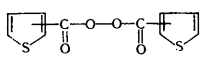
† The calibration $\rho_{RM} = -1$ corresponds to the Alfrey–Price scale for the polar constants of substituents, which are proportional to the Hammett constants[33,34].

composition down. An analogous effect can be observed in the decomposition of saturated per-esters: when chlorine in the α-position to a carbonyl group is replaced by an isopropyl group, the decomposition rate constant increases fourfold[39]. It can also be concluded from these observations that increase in the acceptor properties of radicals should increase their activity in recombination reactions.

Table 2. Decomposition of substituted benzoyl peroxides.

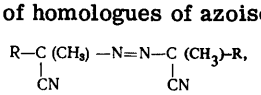
Substituent	10^4k, s^{-1} (at 90°C), from Ref.		
	37	36	38
p-CH_3O	3.29	3.92	5.20
p-CH_3	1.93	2.05	1.98
H	1.33	1.41	1.44
p-Cl	0.94	1.21	1.28
m-Br	1.00	0.81	—
3,4-Dichloro-	1.11	—	—
p-CN	0.97	0.68	0.81
p-NO_2	0.87	—	1.45

An accelerating action of electron-donor substituents has been observed[40] in the decomposition of substituted dithenoyl peroxides of general formula

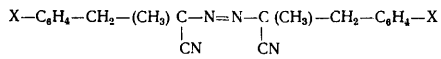


The observed relations are consistent with the tendency of the energy of the O–O bond, which is equal to the activation energy for decomposition of the peroxide, to decrease on passing from hydrogen peroxide to alkyl peroxides[41].

Several investigations[42–44] have been made on the effect of substituents on the decomposition of azo-compounds. Overberger et al.[43] found that the effect of substituents on the decomposition of homologues of azoisobutyronitrile

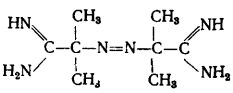


where R = CH_3, C_2H_5, n-C_3H_7, iso-C_4H_9, can be explained by steric causes. In another investigation Overberger and his coworkers[42] found that the substituent in compounds of the type



where X = Cl, H, NO_2, has a weak polar effect.

The substituent has been found to have a considerable effect in the thermal decomposition (at 60–85 °C of azoisobutyramidine



and its nitrates[44]. The addition of one molecule of nitric acid produces a very considerable increase in the rate of decomposition of this compound. Addition of a second molecule of the acid also leads to an increase in the rate of decomposition, but the effect is less marked. Decomposition of the azo-compound and its salts apparently takes place entirely by a radical mechanism, since, when the reaction is conducted in the presence of methyl methacrylate, the latter polymerises at a rate which parallels the rate of decomposition. Since the addition of acid to an amidino-group is equivalent to increasing the electron-acceptor properties of the substituent, the effect of the polarity of the substituent on the decomposition of this compound is formally opposite to the effect of substituents on the decomposition of peroxides, which appears improbable. A possible explanation of the accelerated decomposition of azoisobutyramidine on interaction with an acid is an increase in energy of conjugation in the substituent, which tends to stabilise the radicals and hence diminish the energy of the C–N bond.

IV. EFFECT OF THE MEDIUM ON RADICAL ADDITIONS AND SUBSTITUTIONS

The interaction of radicals with the medium, by which will be understood any set of molecules which do not react directly, including one complexing molecule, can take place in two ways—(1) by interaction of the atom carrying the unsatisfied valency with the medium, and (2) by interaction of substituents on the radical with the medium. A recent review[45] has discussed several radical reactions in which the effect of the medium is evident. In the present Review the effect of the medium is examined as a function of the structure of the radicals and the molecules.

There are few investigations in which the direct effect of the medium on an atom carrying the unpaired electron has been observed experimentally. Most of the systems described relate to reactions in which the radical is a free or substituted heteroatom, e.g. Cl or RO, having a lone pair of electrons directly on the atom containing the unpaired electron. Interaction of such radicals with the medium takes place mainly either by a mechanism of hydrogen bonding or by complex formation with the π-bonds of the solvent. The complicated electronic structure of radicals does not allow the nature of the interaction to be determined unambiguously[45]. Russell[46], who observed that the aromatic character of the solvent influenced the reactivity of the chlorine atom, suggested that a linear relation should exist between the ionisation potential of the radical and the energy of its interaction with the solvent. Investigations of the reactivity of the chlorine atom and of the t-butoxy-radical showed that in aromatic solvents the activity of the radicals diminished with increase in the basic character of the medium. It is significant that the effect of the solvent is considerably more strongly developed on the chlorine atom than on the alkoxy-radical[46,47]. Other investigations[48,49] on the effect of solvents on the activity of the t-butoxy-radical showed a considerably stronger solvent effect. However, while investigating the reaction of the t-butoxy-radical with substituted toluenes in different solvents, Sakurai and Hosomi concluded[49] that the solvent, although strongly influencing the ratio of the rate constant for reaction of the radical with toluenes to the rate constant for decomposition of the t-butoxy-radical into acetone and a methyl radical‡, has little effect on the value of ρ in a series of reactions. Thus values of −0.35, −0.32, and −0.39 were obtained for ρ for Freon-113, chlorobenzene, and acetone at 45°C, whereas the above ratio of the constants for this series of solvents is respectively 2.19, 1.31, and 0.52. From these observations it was concluded[49] that the solvent has a greater effect on the decomposition of the t-butoxy-radical than on its ability to abstract a hydrogen atom. In the opinion of these workers, the effect of the solvent on the reactivity of the radical is described by the variation in ρ with the solvent, and is therefore

‡ The reactivity of the t-butoxy-radicals was determined[47,48] by the method of competing reactions, on the assumption that the decomposition constant of the t-butoxy-radical is independent of the solvent.

small. Investigation of the effect of solvents on the decomposition of oxygen-containing radicals[45] showed that the rate of decomposition of such radicals depended on the presence of hydrogen bonds between the radical and the solvent.

In comparison with heptane, pyridine has been found[50] to have an activating effect, and ethylbenzene a deactivating action, on the reactivity of certain nitric-oxide radicals, in particular on that of the bismethoxyphenylnitrogen oxide radical toward 2,6-di-t-butylphenol. It is assumed[50] that the solvents form π-complexes with the radical. According to spectrophotometric data the heat of complex formation with benzene is 6.2 and 7.5 kcal mole^{-1} in ground and excited states[51].

To ascertain the nature of the effect of the medium it is extremely interesting to examine the action of solvents on the polymerisation and copolymerisation of vinyl monomers, since in this case the atom carrying the radical contains no lone pairs of electrons, which simplifies the pattern of interaction of the radical with the medium. As early as the end of the 1940s the influence of the medium on radical copolymerisation constants was investigated[11] in connection with the parameter e in the $Q-e$ scheme. It was established that copolymerisation constants, measuring the relative activity of the monomers, were independent of the solvent. In particular, such independence was found for the styrene–methyl methacrylate system, copolymerisation of which was conducted in benzene, acetone, and methanol[52]. It follows from these data that the reactivity of hydrocarbon radicals is independent of the properties of the medium. This postulate has become widely accepted, and on its basis vinyl monomers have been classified according to the $Q-e$ parameters[5,11], which represent the reactivity of the monomers. It should be noted that experimental errors in determining the composition of copolymers are fairly substantial, and it is highly probable that the solvent effect will be hidden by these errors. Several investigations have recently been made on the effect of the nature of the solvent on the kinetics of the polymerisation of styrene and methyl methacrylate. In a study of the polymerisation of methyl methacrylate in aromatic solvents, initiated by azoisobutyronitrile, the rate of breakdown of which is practically independent of the solvent[53], Burnett and his coworkers[54] found that the rate of polymerisation increases in the series of solvents—benzene, chlorobenzene, bromobenzene, iodobenzene—by more than 50%. They consider that the solvent, while not affecting the decomposition of the initiator, nevertheless influences the efficiency of initiation by the fact that radicals formed by decomposition of the initiator react with the solvent. In a later paper Burnett et al.[55] have examined the effect of tri- and tetra-halogenated benzenes. It was found that disubstituted benzenes have a greater effect on the rate of polymerisation than have monosubstituted compounds, whereas tri- and tetrasubstituted benzenes have hardly any effect on the rate of polymerisation. In no case was incorporation of the solvent into the polymer observed, which might have indicated an effect of the medium on the reaction by a mechanism of chain transfer. It is curious that the above solvents do not affect the rate of polymerisation when the reaction is initiated by benzoyl peroxide[54]. This supports the view that the solvent influences the efficiency of initiation.

A criticism has recently appeared[56] of the views of Burnett et al. on the mechanism by which the medium affects the polymerisation of methyl methacrylate. The experimental results are confirmed, but it is concluded that the influence of the medium on this process, as on the polymerisation of styrene investigated previously[57], can be explained by the hypothetical formation of a charge-transfer complex between the growing radical and the monomer or the solvent. According to these authors[57] the rate of chain growth V_{gr} is proportional to the concentration of the radical–monomer complex:

$$V_{gr} = K_{gr}[R][M] = K'_{gr}[RM]$$
$$[R] = [RM] + [RS]$$

where R is the free radical, M the monomer, S the solvent, and RM and RS are the complexes formed by the radical with the monomer and with the solvent respectively.

Introducing the mean lifetimes of the complexes τ_M and τ_S and taking into account the stationary state conditions $[RM]/[RS] = \tau_M[M]/\tau_S[S]$, the authors derive an expression for the rate of chain growth:

$$V_{gr} = K_{gr}[R][M] \cdot \varphi^{+}_{gr}, \text{ where } \varphi^{+}_{gr} = \frac{[M]_{S=0}}{[S] \cdot \tau_S/\tau_M + [M]},$$

while $[M]_S = 0$ is the initial concentration of the monomer during bulk polymerisation.

The quantity φ^{+}_{gr} can provide information on the interaction of the radical with the medium. It is determined experimentally from the expression for the rate of polymerisation $V_{pol} = (V_{in}/K_0)^{\frac{1}{2}}[M]\varphi^{+}_{gr}$ or from the corresponding expression for the degree of polymerisation. Using the value obtained for φ^{+}_{gr}, we determine τ_S/τ_M from the relation

$$\frac{[M]_{S=0}}{\varphi^{+}_{gr} \cdot [M]} = 1 + \frac{\tau_S [S]}{\tau_M [M]}.$$

Table 3 gives these authors' results for several solvents.

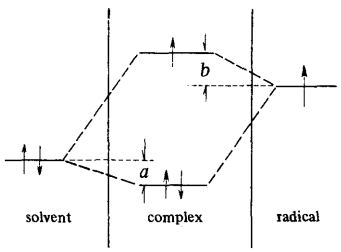
Table 3. Effect of solvents on the polymerisation of styrene (1.82 M at 50°C with azoisobutyronitrile as initiator)[57].

Solvent	φ^{+}_{gr}	τ_S/τ_M	Solvent	φ^{+}_{gr}	τ_S/τ_M
Bromobenzene	1.01	0.93	Dimethylformamide	0.77	0.91
Anisole	0.97	0.97	Toluene	0.77	1.28
Dioxan	0.91	0.87	Methylene chloride	0.72	0.83
Pyridine	0.86	0.87	Tetrahydrofuran	0.7	1.09
Tetrahydropyran	0.9	1.01	Methyl isobutyrate	0.7	1.53
Ethylbenzene	0.84	1.28	Butanone	0.69	1.22
1,2-Dichloroethane	0.84	0.85	Dimethoxyethane	0.66	1.52
Chloroform	0.8	0.90	Ethyl acetate	0.65	1.44
Benzene	0.8	1.04	Styrene	—	1.00
Mesitylene	0.79	1.62			

The idea[57] that the solvent effect is due to complex formation with the radical is supported also by the work of Bamford and Brumby[58], who have investigated the polymerisation of methyl methacrylate in aromatic solvents at 25°C. They find that complex formation influences both the rate constants for chain growth and for chain termination, although the effect is small. Thus the growth rate constant increases from 260 to 330 M^{-1} s^{-1} on passing from benzene to benzonitrile. The diminution in the reaction velocity by solvents parallels their capacity for π-complex formation, and varies in the sequence—benzene > fluorobenzene > chlorobenzene > bromobenzene > benzonitrile.

The tendency of radicals to undergo reactions mainly with aromatic solvents indicates $\pi\pi$-interaction rather than

polar (acceptor or donor) interaction. According to Russell[46] the activity of the chlorine radical falls with decrease in the electronegativity of the substituents in the aromatic solvents. A similar tendency can be observed also in polymerisations. This indicates that the radical acts as an acceptor of electrons in the π-complex. It may be supposed that a π-complex is formed mainly by the superposition of a non-bonding orbital of the radical, in which is located the unpaired electron, with a higher occupied orbital of the solvent, which, as is evident from the diagram, leads to a gain in energy ($E = 2a + b > 0$), and hence a diminution in the activity of the radical. The energy of interaction in the complex is 6 kcal mole^{-1}.[59] However, experimental data indicate the almost complete absence of delocalisation over the solvent of the unpaired electron in complexes of stable radicals with solvents[45], which is inconsistent with participation of the non-bonding orbital of the radical in formation of the complex.



Formation of complex between radical and solvent.

A very curious effect of organoboron compounds on the polymerisation of vinyl monomers has been reported[60,61]: Arimoto[60] discovered that, in the presence of aliphatic organoboron compounds, polymerisation of the monomers—styrene, methyl methacrylate, acrylonitrile, and vinyl acetate—is not inhibited by typical inhibitors of radical processes, e.g. quinol, *N*-phenyl-2-naphthylamine, etc., even when present in excess relative to the organoboron compound. He suggests that the radical forms a complex with the organoboron compound. This complex is reactive towards the monomer and inactive towards inhibitors. Triarylborons do not produce such effects.

The effect of hydrogen bonds on the reactivity of radicals localised on heteroatoms has been examined in a review[45], where it is stated that "... in all cases, when a radical forms hydrogen bonds with those molecules with which it does not react, the result is a decrease in its reactivity in the main reaction". The decreased activity of the radicals must evidently be attributed to steric causes, since, owing to the predominance of electrostatic forces in a hydrogen bond, the energy of the ground state of the radical is lowered, and consequently its reactivity is increased. A solvating molecule impedes the access of reactant molecules to the radical, thereby diminishing the reaction velocity.

Hydrogen bonds have been found to influence the kinetics of radical reactions in the polymerisation of several vinyl monomers containing heteroatoms. On complex formation between the monomer and a hydroxylated solvent through a heteroatom, the change in electronegativity of the heteroatom in the monomer produces a change in the charge distribution, which leads to a change in the polar properties of the double bond and in some cases a change in the conjugation energy. When the monomer becomes a radical as a result of the reaction, the energy of the hydrogen bond is somewhat modified, which complicates interpretation of available results. However, this effect is apparently small, and the characteristics of atoms involved in the hydrogen bond can be assumed to remain unchanged during the reaction. This permits the application to these systems of various correlation formulae.

As remarked above, the composition of copolymers of styrene with methyl methacrylate is unaffected by changing the medium from benzene and acetonitrile to methanol, which indicates that hydrogen bonds have no effect on the reactivity of methyl methacrylate[52]. The rate of polymerisation of *N*-vinylpyrrolidone is increased by conducting the process in aqueous solution, which produces an increase in molecular weight[62], this indicating either a change in the rate constant of chain growth or a decrease in the rate constant of chain termination. Direct experimental evidence of a change in the reactivity of monomers and the corresponding radicals on formation of hydrogen bonds with the solvent was obtained by Ryabov and his coworkers[63]. They found that the composition of styrene–2-vinylpyridine, styrene–methacrylic acid, and methyl methacrylate–methacrylic acid copolymers depends on the nature of the solvent. Subsequent investigations by other workers[64,65] have confirmed these observations. The published data are listed in Table 4. They show that the monomers—vinylpyridines and vinylpyrrolidone—which are electron donors with respect to hydroxylated solvents, are characterised by an increase in the acceptor properties of the substituent (increase in e) with increase in the acidity of the solvent. Acrylic and methacrylic acids, on the other hand, exhibit a diminution in electron-acceptor properties with increase in the basic strength of the solvent. Variation in the properties of the solvent probably affects also the value of Q, which in most cases increases with increase in e. However, this tendency is not clearly defined, and for several systems (Table 4) Q remains unchanged with variation in e. The change in Q produced by varying the solvent indicates that variation in the polarity of the substituent leads to a change in the energy of conjugation in the monomer: i.e. Q and e are not independent quantities, as is assumed in the Q–e scheme. However, these observations require confirmation.

In several cases the rate of polymerisation of monomers has been found to vary with the properties of the medium. Thus the rate of homopolymerisation of methacrylic acid diminishes on the addition of dimethylformamide[63]. Increase in the pH of the medium has been found[68] to decrease the rate constant of chain growth K_{gr} in the polymerisation of acrylamide. The rate of polymerisation of this monomer depends also on the nature of the solvent[59]: the value of $K_{gr}/K_0^{\frac{1}{2}}$ decreases in the sequence—water, dimethyl sulphoxide, tetrahydrofuran. The reason for the change in the rate of polymerisation of *N*-vinylpyrrolidone when dichloroethane is replaced by methanol is the change in K_{gr} due to the diminished electron-donor properties of the pyrrolidone ring. The observed doubling of K_{gr} shows good qualitative correlation with Eqn. (4).

Several interesting results have recently been obtained on the effect of metal salts on the activity of monomers in radical polymerisation. As early as 1957 Bamford et al.[69] reported that a lithium salt accelerates the polymerisation

of acrylonitrile. Several papers have since been published on the influence of salts of zinc [70-75], cadmium [74], mercury [73], and aluminium [76-78].

Table 4. Effect of hydrogen bonds on reactivity of monomers in copolymerisations.

Monomers M_1	Monomers M_2	Solvent	r_1	r_2	Q_2	e_2	Ref
Styrene $Q=1$ $e=-0,8$	2-vinylpyridine	—	0.57	1.33	(1.16)	(−0.285)*	63
		ethanol	0.486	0.862	(0.55)	(0.13)	63
		methanol					
		phenol	0.426	0.607	(0.93)	(0.36)	63
		acetic acid	0.253	0.549	(1.29)	(0.6)	63
			0.16	0.36	(1.62)	(0.89)	6
Styrene	4-vinylpyridine	—	0.78	1.1	1.12	−0.72	66
		acetic acid	0.1	0.34	3.1	1.35	66
Methyl methacrylate	ditto	—	0.42	0.65			66
		acetic acid	0.24	0.55			66
ditto	2-vinylpyridine	—	0.48	0.68	1.35	−0.7	66
		acetic acid	0.43	0.3	1.80	1.3	66
Styrene	methacrylo-2,5-methylvinylpyridine	—	0.88	1.1	1.1	−0.8	66
		acetic acid	0.73	0.76	1.0	−0.2	66
Methyl methacrylate	ditto	—	0.42	0.58			66
		acetic acid	0.47	0.75			66
Styrene	methacrylic acid	—	0.2	0.66	(1.60)	(0.62)	63
		dimethylformamide	0.53	0.45	(0.73)	(0.4)	63
Methyl methacrylate $Q=0.74$ $e=0.4$	ditto	—	0.55	1.55	(1.58)	(0.8)	63
Methyl methacrylate $Q=0.74$ $e=0.4$	methyl methacrylate	dimethylformamide	0.98	0.68	(0.59)*	(−0.24)	63
Styrene	acrylic acid	—	0.25	0.07	0.94	1.01	64, 65
		butan-2-one	0.7	0.15			
		dioxan	0.75	0.13	0.39	0.73	64, 65
		tetrahydrofuran	0.9	0.14	0.35	0.64	64, 65
		dimethylformamide	1.03	0.15	0.33	0.57	64, 65
Methyl methacrylate	ditto	—	1.86	0.24	0.31	0.81	64, 65
		benzene	1.5	0.2			
		dioxan	2.32	0.3	0.25	0.65	64, 65
		tetrahydrofuran	2.46	0.25	0.24	0.61	64, 65
		dimethylformamide	2.89	0.24	0.2	0.51	64, 65
Vinyl chloride	*N*-vinylpyrrolidone	dichloroethane	0.55	0.34	0.066	−1.1	67
		methanol	0.74	0.73	0.052	−0.6	67

*Values in parentheses have been calculated by me from the values given for r_1 and r_2.

Imoto and his coworkers [70,71] have found that during polymerisation methyl methacrylate forms an active complex MMA.$ZnCl_2$ in the presence of zinc chloride. Copolymerisation constants have been determined for this complex with vinylidene chloride, whose activity is unaffected by zinc chloride, and the parameters Q and e have been calculated (Table 5). These workers have investigated also the effect of zinc chloride on the polymerisation of acrylonitrile.

Okamura and his coworkers [73-75] have made a series of studies of the effect of complex formation with metal salts on the reactivity of vinylpyridines. They find that complexes are formed containing two molecules of the monomer and one molecule of the salt. The rate of polymerisation of the complex is higher than that of the pure monomer. The increase in rate is assumed to be due to an increase in K_{gr}. For 4-vinylpyridine the accelerating effect increases in the sequence [74]

$$Cd(CH_3COO)_2 > ZnCl_2 > Zn(CH_3COO)_2 > ZnBr_2 > ZnI_2$$

which is almost the same as the sequence for 2-methyl-5-vinylpyridine [73]. Values of Q and e for vinylpyridines included in Table 5, have been determined for copolymerisation with styrene, which does not form complexes with metal salts.

Table 5. Effect on the reactivity of monomers of complex formation with metal salts.

M_1	M_2	T, °C	r_1	r_2	Q_1	e	Ref.
MMA*	CH_2CCl_2	60	2.5	0.5	0.74	0.4	71
MMA + 0.089 $ZnCl_2$	ditto	60	12	0.08	2.82	0.8	71
MMA + 0.214 $ZnCl_2$	»	60	20	0.04	6.63	1.1	71
4-VP**	styrene	50	0.52	0.54	0.82	−0.2	74
4-VP + $Zn(CH_3COO)_2$	ditto	50	2.7	0.08	4.7	0.44	74
2-VP	»	50	0.9÷1.81	0.55	1.3	−0.5	74
2-VP + $Zn(CH_3COO)_2$	»	50	3.55	0.55	$r_1 \cdot r_2 =$	1.84>1	74
2-Methyl-5-VP	»	50	0.68	0.6÷0.88	0.99	−0.58	74
2-Methyl-5-VP + + $Zn(CH_3COO)_2$	»	50	2.0	0.35	1.75	−0.26	74

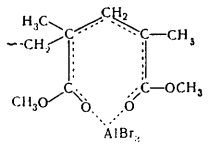
*MMA = methyl methacrylate.
**VP = vinylpyridine.

Direct confirmation of the increase in K_{gr} on complex formation between methyl methacrylate and zinc chloride has been obtained by Bamford et al. [79], who find that at 25°C the value of K_{gr} increases from 250 $M^{-1}\,s^{-1}$ for the pure monomer to 610 $M^{-1}\,s^{-1}$ for its complex.

A characteristic feature of the monomer–metal salt complexes investigated is the simultaneous increase in the parameters Q and e relative to the pure monomer (Table 5). This indicates the complicated nature of the interaction between metal salts and monomers, caused by the formation of a single system of molecular orbitals in the complex compound. Examination of the electronic absorption spectra showed that the complexes exhibit a red shift in the $\pi-\pi$ transition as compared with the pure monomer [75]. The magnitude of the displacement correlates with the value of Q. An attempt has been made to examine the structure of the complexes by the method of molecular orbitals [94].

The effect of Lewis acids on the reactivity of monomers has been investigated in the copolymerisation of acrylonitrile and methyl methacrylate [76,77]. Addition of aluminium chloride led to a decrease in the acrylonitrile content of the copolymer. The complex of acrylonitrile with aluminium chloride proved to be incapable of homopolymerisation, which must apparently be attributed to electrostatic repulsion between the radical and the monomer. The photoinitiated polymerisation of methyl methacrylate in the presence of aluminium chloride and aluminium bromide revealed [78] a considerable increase in the rate of the process compared with polymerisation of the pure monomer, which was ascribed to increase in K_{gr} due to the coordinating action of the aluminium salt. Use of electron spin resonance in the same investigation established that the unpaired electron is

partly transferred to the aluminium atom. The following scheme is suggested [78] for the transition state in chain growth



according to which growth is accelerated by coordination of the monomer and the radical.

The interaction of acrylonitrile with ethylaluminium dichloride [80] leads to the formation of a 1 : 1 complex. It is remarkable that the complex is incapable of homopolymerisation, but copolymerises well, e.g. with propene to form an alternating 1 : 1 copolymer. The alternation may be caused by the formation of a charge-transfer complex between the monomers. The possibility of the formation of such complexes must in general be taken into account in ascertaining their reactivity, since considerable anomalies may be observed. For example, it has proved possible to copolymerise 1,4-dioxen with maleic anhydride [81], although neither monomer polymerises separately by a radical mechanism; their copolymerisation was made possible by complex formation.

Thus the polar effect of the medium on the reactivity of radicals and molecules, effected through hydrogen bonds, complex formation with metal salts, etc., can be identified with the change in the properties of the substituents, and described by Eqn. (4). The nature of the change in the energy of radicals on π-complex formation with solvents and on interaction with electron pair acceptors, such as organoboron compounds, is obscure. It may be supposed that π-complex formation is accompanied by a decrease in the energy of the radical caused the solvent utilising a non-bonding orbital of the radical.

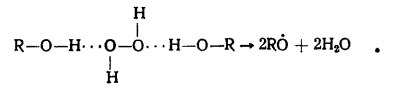
V. EFFECT OF SOLVENTS ON THE THERMAL DECOMPOSITION OF AZO-COMPOUNDS AND PEROXIDES

The influence of solvents on the unimolecular decomposition of molecules has been investigated on the decomposition of peroxides and azo-compounds, which are initiators of various radical processes.

Arnett [82] investigated the thermal decomposition of azoisobutyronitrile in various solvents, and found the rate constant to vary little with the solvent. In a thorough investigation Morou [53] also detected only a slight variation in the rate constant for the decomposition of azoisobutyronitrile with the nature of the solvent. Thus in the series of solvents—methyl methacrylate, xylene, cyclohexanol, dioxan, *o*-dichlorobenzene, and dimethylformamide—the decomposition rate constants at 60°C were respectively (8.40, 10.40, 12.5, 8.70, 11.0, and 10.94) $\times 10^{-6}$. Because of the unsystematic collection of solvents, these results are insufficient to determine the effect of solvents. An attempt to interpret the effect of solvents on the decomposition of phenylazotriphenylmethane was unsuccessful [83].

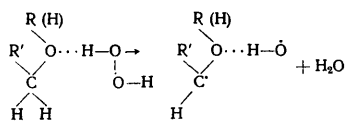
The effect of solvents on the decomposition of benzoyl peroxide is discussed in Bagdasar'yan's monograph [5]. Analysis of the experimental data shows that this compound tends to undergo chain decomposition. At low concentrations of the peroxide or in the presence of inhibitors the decomposition rate constant is almost independent of the solvent. An appreciable solvent effect is observed in the decomposition of t-butyl 2,3-dipropylcycloprop-2-eneper-carboxylate [84]. The rate of decomposition increases in the sequence—ethylbenzene, chlorobenzene, benzonitrile, acetonitrile, benzyl alcohol.

Complicated phenomena are observed in the decomposition of hydroperoxides, including hydrogen peroxide, in various solvents. The energy of the O–O bond is 48 kcal mole^{-1} in hydrogen peroxide [85], and rather lower (42 kcal mole^{-1}) in aliphatic hydroperoxides [41]. In an investigation of the thermal decomposition of butyl and cumene hydroperoxides Stannett and Mesrobian [86] observed an accelerating effect with alcohols, ethers, acids, and vinyl monomers in comparison with benzene, cyclohexane, carbon tetrachloride, chloroform, chlorobenzene, and even pyridine. The authors did not suggest any mechanism to explain the effect of the solvents. Later investigation of the decomposition of hydroperoxides [87–93] have yielded additional data enabling the reaction mechanism to be assessed to a certain extent. It was ascertained that in active solvents the activation energy of the decomposition of hydroperoxides is lowered to around 20 kcal mole^{-1}, [88–92] which is 15–20 kcal mole^{-1} lower than the value in the gas phase and apparently in inert solvents [41,85]. To explain such a large energy discrepancy it has been suggested [88,89] that in alcohol it is not a hydroperoxide molecule but its complex with the solvent which decomposes:



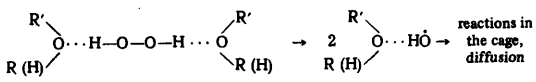
According to this scheme simultaneous cleavage of three bonds and the formation of two new bonds take place in the activated complex. The scheme provides an explanation of the decrease in activation energy of decomposition, but is inconsistent with the formation of terminal hydroxy-groups in the oligodienes obtained by initiating the polymerisation of dienes with hydrogen peroxide in methanol [91].

It was also found [91] that replacing the alcohol by tetrahydrofuran has little effect on the rate or the efficiency of initiation, but substantially affects the concentration of hydroxyls in the polymer. In the opinion of the authors the following scheme for the transition state



which takes into account solvation of the peroxide by the solvent, enables the observed phenomena to be understood. According to this scheme the low efficiency of initiation is explained by the abstraction of α-hydrogen atoms from the solvent and subsequent recombination of the resulting radicals in the cage. The diminished concentration of hydroxyls in the polymer is also explained by instantaneous transfer of the radical to the solvent on formation. Since the transfer reaction is exothermic, and can occur at the same time as cleavage of an O–O bond, the decrease in activation energy for decomposition of the peroxide can also be explained. According to later, unpublished results obtained by the same workers [91], however, polymerisation of dienes initiated by hydrogen peroxide is observed also in solution in t-butyl alcohol which has no α-hydrogen atom, and occurs at the same rate as in methyl alcohol, leading to the formation of oligomers containing two terminal hydroxy-groups. This indicates that abstraction of an α-hydrogen atom is independent of cleavage of the O–O bond.

With all the above facts taken into account, the suggestion is made that hydrogen peroxide (and hydroperoxides) decompose according to the scheme



the realisation of which requires that the energy of interaction of the hydroxyl radical with the heteroatom of the solvent should be increased by 10–15 kcal mole^{-1} as compared with the energy of a hydrogen bond. This increase in interaction energy is possible as a consequence of the formation of complexes analogous to charge-transfer complexes or π-complexes (see diagram).

Acceleration of the decomposition of hydroperoxides is observed also in hydrocarbon solvents containing double bonds[89-93]. The acceleration apparently results mainly as a consequence of the reaction

$$ROOH + H_2C{=}CHR_1 \rightarrow HOCH_2{-}\dot{C}HR_1 + \dot{O}R$$

suggested by Denisov[92], in which the vinyl compound acts as an electron donor. Walling and Heaton[93] found styrene oxide, t-butyl alcohol, and water among the products of the reaction of t-butyl hydroperoxide with styrene, and assumed that decomposition of a hydroperoxide partly involves cleavage of the O–H bond:

$$ROOH + CH_2{=}CHR' \rightarrow R\dot{O}O + CH_2\dot{C}HR' .$$

When the polymerisation of isoprene is initiated with cumene hydroperoxide in heptane solution, the polymeric products are found to contain on the average one hydroxy-group per macromolecule[91], which confirms Denisov's scheme.

From the above results on the effect of solvents on the decomposition of hydroperoxides and hydrogen peroxide it can be seen that all solvents which accelerate the decomposition contain either heteroatoms having lone pairs of electrons or π-bonds: i.e. they are donors of electrons relative to hydroxy-groups. Some analogy is evident in the effect of solvents on the reactivity of radicals in reactions involving hydrogen atom abstraction, which have become known from the work of Russell[46], and in the decomposition of hydroperoxides. This analogy has a single cause—the diminution in the reactivity of radicals on complex formation with the solvent.

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The analysis which has been made of various radical reactions shows that the reactivity of radicals and molecules is considerably influenced by polar interactions of the reaction centre with substituents and with the medium. With few exceptions the reactivity of radicals is increased by the introduction of electron-acceptor substituents and by increase in the acidity of the medium or decrease in the electron-donor properties of the solvent. The opposite relations are observed for molecules.

REFERENCES

1. F. London, Ztschr. Elektrochem., 35, 552 (1929).
2. S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes" (Translated into Russian), Inostr. Lit., Moscow, 1948, p. 99.
3. N. N. Semenov, "O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti" (Some Problems of Chemical Kinetics and Reactivity), Moscow, 1958.
4. Yu. L. Spirin, Zhur. Fiz. Khim., 36, 1202 (1962) [Russ. J. Phys. Chem., No. 6 (1962)].
5. Kh. S. Bagdasar'yan, "Teoriya Radikal'noi Polimerizatsii" (Theory of Radical Polymerisation), Nauka, Moscow, 1966.
6. K. O'Driscoll and T. Yonezawa, Khim. Tekhnol. Polimerov, No. 7, 3 (1967) (Translated into Russian).
7. A. Streitweiser, "Molecular Orbital Theory" (Translated into Russian), Mir, Moscow, 1965.
8. M. V. Bazilevskii, Dokl. Akad. Nauk SSSR, 172, 881 (1967).
9. C. D. Ritchie and W. F. Sager, Progr. Phys. Org. Chem., 3, 323 (1965).
10. V. A. Pal'm, "Osnovy Kolichestvennoi Teorii Organicheskikh Reaktsii" (Foundations of a Quantitative Theory of Organic Reactions), Khimiya, Moscow, 1967.
11. T. Alfrey, J. J. Bohrer, and H. Mark, "Copolymerisation" (Translated into Russian), Inostr. Lit., Moscow, 1953, p. 114.
12. G. H. Williams, Progr. Stereochem., 2, 39 (1958).
13. R. L. Huang and K. H. Lee, J. Chem. Soc., C10, 935 (1966).
14. G. A. Russell, J. Amer. Chem. Soc., 78, 1047 (1956).
15. K. M. Jonston and G. H. Williams, J. Chem. Soc., 1446 (1960).
16. E. Kalatzis and G. H. Williams, J. Chem. Soc., B11, 1112 (1966).
17. M. Imoto and M. Kinosita, Makromol. Chem., 86, 217 (1965).
18. T. Otsu, T. Ito, T. Fukumizu, and M. Imoto, Bull. Chem. Soc. Japan, 39, 2257 (1966).
19. T. Otsu, T. Ito, and M. Imoto, J. Polymer Sci., B3, 113 (1965).
20. J. I. G. Cadogan and I. H. Sandler, J. Chem. Soc., B12, 1191 (1966).
21. T. Yamamoto, Bull. Chem. Soc. Japan, 40, 642 (1967).
22. J. A. Howard and K. U. Ingold, Canad. J. Chem., 41, 1744 (1963).
23. V. D. Pokhodenko and V. A. Bidzilya, Teor. Eksper. Khim., 2, 691 (1966).
24. V. A. Bidzilya, V. D. Pokhodenko, and A. I. Brodskii, Dokl. Akad. Nauk SSSR, 166, 1099 (1966).
25. K. U. Ingold, Canad. J. Chem., 41, 2816 (1963).
26. T. Otsu, T. Ito, and M. Imoto, J. Chem. Soc. Japan, Ind. Chem. Sect., 69, 986 (1966).
27. T. Yamamoto, T. Otsu, and M. Imoto, J. Chem. Soc. Japan, Ind. Chem. Sect., 69, 990 (1966).
28. M. Anbar, D. Meyerstein, and P. Neta, J. Phys. Chem., 70, 2660 (1966).
29. M. Anbar, D. Meyerstein, and P. Neta, Nature, 209, 1348 (1966).
30. R. Ito, T. Migita, N. Morikawa, and O. Simamoto, Tetrahedron, 21, 955 (1965).
31. Yu. L. Spirin, Kinetika i Kataliz, 8, 38 (1967).
32. Yu. L. Spirin, Vysokomol. Soed., 10A, 1699 (1968).
33. J. Furukawa and T. Tsuruta, J. Polymer Sci., 36, 275 (1959).
34. T. Tsuruta, "Reactions in the Preparation of Synthetic Polymers" (Translated into Russian), Goskhimizdat, Moscow, 1963, p. 87.
35. A. R. Gantmakher, Yu. L. Spirin, and S. S. Medvedev, Vysokomol. Soed., 1, 1526 (1959).
36. C. G. Swain, W. H. Stockmayer, and J. T. Clarke, J. Amer. Chem. Soc., 72, 5426 (1950).
37. K. F. O'Driscoll and P. J. White, J. Polymer Sci., A3, 283 (1965).
38. A. T. Blomquest and A. J. Buseli, J. Amer. Chem. Soc., 73, 3883 (1951).

39. S. S. Ivanchev, Doctoral Thesis, Odessa State University, 1968.
40. R. D. Smetz, F. M. Gruen, D. R. Burne, and R. L. Brennan, J. Heterocycl. Chem., 3, 184 (1966).
41. S. W. Benson, J. Chem. Phys., 40, 1007 (1964).
42. C. G. Overberger and H. Biletch, J. Amer. Chem. Soc., 73, 4880 (1951).
43. C. G. Overberger, M. T. O. Shaughnessy, H. Shalit, J. Amer. Chem. Soc., 71, 2661 (1949).
44. G. S. Hammond and R. C. Neuman, J. Amer. Chem. Soc., 85, 1501 (1963).
45. A. L. Buchachenko and O. P. Sukhanova, Uspekhi Khim., 36, 192 (1967) [Russ. Chem. Rev., No. 3 (1967)].
46. G. A. Russell, J. Amer. Chem. Soc., 80, 4987 (1958); 86, 2357 (1964).
47. G. A. Russell, J. Org. Chem., 23, 1407 (1958); 24, 300 (1959).
48. C. Walling and P. Wagner, J. Amer. Chem. Soc., 85, 2333 (1963).
49. H. Sakurai and A. Hosomi, J. Amer. Chem. Soc., 89, 458 (1967).
50. A. L. Buchachenko O. P. Sukhanova, L. A. Kalashnikova, and M. B. Neiman, Kinetika i Kataliz, 6, 601 (1965).
51. L. A. Kalashnikova, M. B. Neiman, and A. L. Buchachenko, Zhur. Fiz. Khim., 42, 1144 (1968) [Russ. J. Phys. Chem., No. 5 (1968)].
52. F. M. Lewis, C. Walling, W. Cummings, E. Briggs, and F. R. Mayo, J. Amer. Chem. Soc., 70, 1519 (1948).
53. A. F. Morou, Makrom. Chem., 105, 43 (1967).
54. D. B. Anderson, G. M. Burnett, and A. C. Gowan, Second International Symposium on Macromolecular Chemistry, Moscow, 1960, p. 111.
55. G. M. Burnett, W. S. Dailing, and J. M. Pearson, Trans. Faraday Soc., 61, 1916 (1965).
56. G. Henrici-Olive and S. Olive, Makromol. Chem., 96, 221 (1966).
57. G. Henrici-Olive and S. Olive, Ztschr. Phys. Chem., 47, 286 (1965); 48, 35 (1966).
58. C. H. Bamford and S. Brumby, Makromol. Chem., 105, 122 (1967).
59. V. F. Gromov, A. V. Matveeva, A. D. Abkin, P. M. Khomikovskii, and E. I. Mirokhina, Dokl. Akad. Nauk SSSR, 179, 374 (1968).
60. F. S. Arimoto, J. Polymer Sci., 4A, 275 (1966).
61. R. I. Kern and S. Jacob, J. Polymer Sci., 5B, 157 (1967).
62. I. V. Braitenbakh, in Collected Papers, "Chemie und Technologie der Kunstoffe", Edited by R. Houwink and A. Staverman, (Translated into Russian) Khimiya, Moscow, 1965, Vol. 1, p. 266.
63. A. V. Ryabov, Yu. D. Semchikov, and N. N. Slavitskaya, Dokl. Akad. Nauk SSSR, 145, 822 (1962); 154, 1135 (1964).
64. R. Kerber, Makromol. Chem., 96, 30 (1966).
65. R. Kerber and H. Glamann, Makromol. Chem., 100, 290 (1967).
66. Yu. D. Semchikov, A. V. Ryabov, and V. N. Kashaeva, Vysokomol Soed., 10B, 57 (1968).
67. Yu. L. Spirin and T. S. Yatsimirskaya, Vysokomol. Soed., in the press.
68. D. I. Currie, F. S. Dainton, and N. S. Watt, Polymer, 6, 451 (1965).
69. C. H. Bamford, A. D. Jenkins, and R. Johnston, Proc. Roy. Soc., A241, 364 (1967).
70. M. Imoto, T. Otsu, and S. Shimizu, Makromol. Chem., 65, 174 (1963).
71. T. Otsu and Y. Harada, Makromol. Chem., 65, 180 (1963).
72. M. Imoto, T. Otsu, B. Yamada, and A. Shimizu, Makromol. Chem., 82, 277 (1965).
73. S. Tazuke, N. Sato, and S. Okamura, J. Polymer Sci., 4AI, 2461 (1966).
74. S. Tazuke and S. Okamura, J. Polymer Sci., 5AI, 1083 (1967).
75. S. Tazuke and S. Okamura, J. Polymer Sci., B5, 95 (1967).
76. H. C. Haas and F. K. Kariln, J. Polymer Sci., 9, 588 (1952).
77. H. C. Haas, Makromol. Chem., 80, 232 (1964).
78. V. P. Zubov, M. B. Loginov, L. I. Valuev, V. D. Golubev, V. A. Kabanov, and V. A. Kargin, Vysokomol. Soed., 9B, 667 (1967).
79. C. H. Bamford, S. Brumby, and R. P. Wayne, Nature, 209, 292 (1966).
80. M. Hirooka, H. Yabunchi, S. Morita, S. Kawasumi, and K. Nakaguchi, J. Polymer Sci., B5, 47 (1967).
81. S. Iwatsuki and Y. Jamashita, Makromol. Chem., 89, 205 (1965).
82. L. Arnett, J. Amer. Chem. Soc., 74, 2027 (1952).
83. N. G. Bentrude and A. K. Macknight, Tetrahedron Letters, 3147 (1966).
84. C. Ruchardt and H. Schwarzer, Chem. Ber., 99, 1871 (1966).
85. V. I. Vedeneev et al., "Energii Razryva Khimicheskikh Svyazei" (Energies of Rupture of Chemical Bonds), Izd. Akad. Nauk SSSR, Moscow, 1962.
86. V. Stannett and R. S. Mesrobian, J. Amer. Chem. Soc., 72, 4125 (1950).
87. M. G. Privalova, Z. K. Maizus, and N. M. Emanuel', Dokl. Akad. Nauk SSSR, 161, 1135 (1965).
88. E. T. Denisov and V. V. Kharitonov, Kinetika i Kataliz, 5, 781 (1964).
89. N. M. Emanuel', E. T. Denisov, and Z. K. Maizus, "Tsepnye Reaktsii Okisleniya Uglevodorodov v Zhidkoi Faze" (Chain Oxidations of Hydrocarbons in the Liquid Phase), Nauka, 1965.
90. B. A. Redoshkin and V. A. Shushunov, Collected Papers, "Khimiya Perekisnykh Soedinenii" (Chemistry of Peroxide Compounds), Izd. Akad. Nauk SSSR, Moscow, 1963, p. 207.
91. V. K. Grishchenko and Yu. L. Spirin, Vysokomol. Soed., 11A, 980 (1969).
92. E. T. Denisov and L. N. Denisova, Dokl. Akad. Nauk SSSR, 157, 907 (1964).
93. C. Walling and L. Heaton, J. Amer. Chem. Soc., 87, 38 (1965).
94. S. Tazuke, K. Tsuljik, T. Yonesawa, and S. Okamyra, J. Phys. Chem., 71, 2957 (1967).

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