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HYDROGEN BONDS AND π-COMPLEXES IN RADICAL LIQUID-PHASE REACTIONS

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1. INTRODUCTION

The investigation of the influence of the solvent on the kinetics of radical liquid-phase reactions is of considerable importance for the theory of reactivity. The interaction of a reacting species with solvent molecules alters the electronic structure and reactivity of the species. From a knowledge of this interaction it is possible to obtain important information about the factors influencing the reactivity of the reacting species. There is, moreover, another practical aspect of this problem, associated with the choice of solvent and the improvement of technological processes.

The strongest specific interactions exerting a significant influence on the kinetics and sometimes also the mechanism of liquid-phase radical reactions are those revealed in hydrogen bonds and π-complexes. The aim of the present review is to examine the part played by these interactions in kinetics and to reveal their nature and mechanism, that is to analyse the structural-kinetic aspect of specific interactions.

2. HYDROGEN BONDS IN RADICAL REACTIONS

The problem of the part played by hydrogen bonds in the kinetics of chemical reactions was first raised by Emanuel'.[1] A later review[2] examined a large amount of material on the influence of hydrogen bonding on the kinetics and mechanism of many reactions (chiefly ionic). Numerous studies carried out since that time have confirmed conclusively that the manifestation of hydrogen bonding is one of the fundamental characteristics of liquid-phase kinetics. Much of the mechanism by which hydrogen bonding affects the rate of radical reactions is not yet clear, however.

It is first of all important to know whether a reaction takes place through equilibria involving the association of the reacting species by hydrogen bonding and if so, which of the constants of the multi-stage equilibrium are important. It is possible that the reaction involves not only free non-associated molecules, but also solvates, so that hydrogen bonding is also manifested in the activated complex. The coordination number of the solvated complex is then always of considerable importance.

Physical methods of study (X-ray diffraction, electron diffraction, infrared spectroscopy, nuclear magnetic resonance, etc.) make it possible to obtain extensive thermodynamic information on the structure of the solvates, their coordination numbers, and the equilibrium constants for a large number of classes of substances. This material has been collected in a number of reviews and monographs[3-5]. Different methods often give contradictory information on the structure of solvates, but even if the structure of the associated forms is fairly well known, it is difficult to estimate the part which they play in kinetics: for this, kinetic analysis of the influence of association on the reaction rates is necessary.

In radical reactions, each of the participants in the reaction — the molecule and the radical — may be associated. Let us consider first the influence of association of the molecules on the rate of their reactions.

In the study of the decomposition of hydroperoxides, which are the primary products of the oxidation of most organic and many inorganic compounds, it has been established that at sufficiently high concentrations of the hydroperoxide, its decomposition obeys the kinetic equation for a first-order reaction and apparently proceeds according to the scheme

$$2ROOH \rightarrow R\dot{O}_2 + H_2O + R\dot{O}. \quad (1)$$

This has been observed in the decomposition of ethyl linoleate[6], cyclohexyl[7], tetralin[8], n-decyl[9], t-butyl[10], and cumene hydroperoxides.

It was assumed that the hydroperoxide molecules are associated by hydrogen bonding to form dimers[6,11], and that their decomposition to give radicals is thereby facilitated considerably. The association of hydroperoxides was in fact confirmed by physical methods[7,12], but kinetic proof of the preferential participation of the associated hydroperoxide in decomposition according to scheme (1) was given only recently in papers by Denisov[10,13]. An analogous effect of increase in the rate of decomposition is brought about by intramolecular hydrogen bonding in acyl hydroperoxides[1].

The decomposition of hydroperoxides is also facilitated by the presence of other substances capable of undergoing association with the hydroperoxide molecules by hydrogen bonding, for example alcohols[14], organic acids[15], etc. This phenomenon was studied in detail[16] for the decomposition of n-decyl hydroperoxide in the presence of hexanoic acid. It is assumed that the decomposition scheme is

$$\mathrm{ROOH} + n\,\mathrm{R'COOH} \overset{K}{\rightleftarrows} (\text{associate}) \overset{k}{\rightarrow} \dot{\mathrm{R}}\mathrm{O} + \dot{\mathrm{O}}\mathrm{H} + n\,\mathrm{R'COOH}. \qquad (2)$$

It was shown that the coordination number n of the associate, that is the number of molecules of acid in the complex with the hydroperoxide, is equal to 2; the equilibrium constants K and the constants k for the decomposition of the complex to form radicals were also determined. The activation energy for the decomposition of the hydroperoxide in the associate (16.1 kcal mole^{-1}) was found to be much less than that for the decomposition of the hydroperoxide in the absence of the acid (23.8 kcal mole^{-1}). All these facts indicate that hydrogen bonding occurs in the elementary stages of the decomposition of the hydroperoxides to form radicals. A detailed analysis of the mechanism of decomposition involving hydrogen bonding, from the viewpoint of the heats and activation barriers of the elementary reactions, was given by Berezin[17].

In radical substitutions (in particular, in the most extensively studied reactions involving hydrogen atom abstraction), the presence of associates of molecules reacting with one another or with solvent molecules by hydrogen bonding means that both free molecules and their associates may take part in the reaction, at different rates. Kinetic proof for this differentiated participation is given in a number of papers.

Thus Berezin's work[17,18] on the oxidative decarboxylation of decanoic acid according to the scheme

$$\mathrm{RCOOH} + \mathrm{r}\dot{\mathrm{O}}_2 \rightarrow \mathrm{r\,OOH} + \mathrm{RC}\!\!<\!\!\begin{matrix}\dot{\mathrm{O}}\\ \mathrm{O}\end{matrix}$$
$$\mathrm{RC}\!\!<\!\!\begin{matrix}\dot{\mathrm{O}}\\ \mathrm{O}\end{matrix} \rightarrow \dot{\mathrm{R}} + \mathrm{CO}_2 \qquad (3)$$

where $\mathrm{rO_2}$ represents the peroxide radical of the hydrocarbon rH in which the decarboxylation takes place, established convincingly that only monomeric non-associated acid molecules take part in the reaction (3), the acid dimers formed by hydrogen bonding being quite inactive.

Study of the reaction of diethyl phosphite with the tri-t-butylphenoxyl radical[19] showed that the effective rate constant for the reaction in benzene increases considerably with decrease in the concentration of phosphite. Kinetic analysis of this dependence showed that the free tri-t-butyl phenoxyl reacts much more rapidly with the monomeric form of the phosphite than with the associated form, the coordination number of which is two. Thus here also the monomeric molecules are found to be much more active than the molecules associated to form dimers.

Hydrogen bonding is revealed most clearly in the kinetics of radical reactions with strongly associated molecules such as alcohols and phenols. The analysis of these reactions has now yielded a sufficiently clear picture of the mechanism and nature of the kinetic influence of hydrogen bonding.

Berezin[17,20] showed that the rate constant for the reaction between the methyl radical and t-butyl alcohol with a tritiated hydroxyl group according to the scheme

$$\dot{\mathrm{C}}\mathrm{H}_3 + (\mathrm{CH}_3)_3\,\mathrm{COT} \xrightarrow{k_{\mathrm{OT}}} \mathrm{CH}_3\mathrm{T} + (\mathrm{CH}_3)_3\,\dot{\mathrm{C}}\mathrm{O} \qquad (4)$$

depends to a marked extent on the concentration of the alcohol in n-heptane; with increase in the alcohol concentration, the reactivity of free methyl with respect to the hydroxyl group decreases sharply. This agrees with the idea that only monomeric t-butyl alcohol molecules react with methyl radicals. Detailed kinetic analysis showed that the associates apparently have a cyclic structure; it was also possible to determine the thermodynamic characteristics of the association equilibrium. This work confirmed earlier qualitative observations that associated hydroxyl groups in alcohols are unreactive[21].

The association of phenols has an analogous influence on the reactivity of their hydroxyl hydrogen atoms with respect to methyl radicals[17]; the same is true of the reactions of phenols and amines with peroxide radicals[22]. The hydroxyl hydrogen of alcohols is also comparatively inert with respect to hydrogen atom abstraction[23].

The influence of the medium on the kinetics of the reactions of nitrophenols with the stable tri-t-butylphenoxyl radical, involving the removal of hydroxyl hydrogen, has also been studied[24,25]. For *o*-nitrophenol, the rate constants for this reaction and the activation energies are quite independent of the nature of the solvent in which the reaction takes place (benzene, hexane, acetone, or methanol), but for *m*-nitrophenol the medium has a marked influence not only on the rate constants but also on the activation energies (Table 1). A linear relationship between the logarithms of the pre-exponential terms and the values of the activation energy, that is a compensation effect, is observed. The compensation effect is apparently due to the influence of the medium; this influence is localised and is determined by the interaction between the reaction centre and the solvent. The dielectric properties of the solvent have no significant influence on the reaction rate constants even for such dipolar species as the phenoxyl radical and phenol; this follows from the data for *o*-nitrophenol. This also indicates, in particular, that the reacting radical is not solvated (apparently because of steric hindrance). Comparison of the results for *o*- and *m*-nitrophenols indicates that the hydroxyl hydrogens of *o*-nitrophenol do not form hydrogen bonds with the solvent because of the steric hindrance created by the nitro-group and also because of the strong intramolecular hydrogen bond. When the acetone or alcohol is diluted with inert solvents (heptane), the

TABLE 1. Pre-exponential factors k_0 and activation energies E for the reaction of *m*-nitrophenol with tri-t-butylphenoxyl.

Solvent	k_0, cm^3 s^{-1}	E, kcal mole^{-1}
Benzene	$8\cdot10^{-16}$	10.2
Acetone	$5\cdot10^{-14}$	14.7
Methanol	$6\cdot10^{-13}$	17.3

m-nitrophenol associates are broken down, yielding the more reactive molecules of the monomeric phenol and a corresponding increase in the effective rate constant[25].

The reaction of a radical with a molecule capable of undergoing solvation can be represented in the following general form:

$$\begin{aligned} \dot{R} + XOH_0 &\xrightarrow{k_0} RH + X\dot{O} \\ \dot{R} + XOH_S &\xrightarrow{k_S} RH + X\dot{O} \\ XOH_0 + nS &\overset{K}{\rightleftarrows} XOH_S \\ X\dot{O} + \dot{R} &\xrightarrow{k_1} XOR \end{aligned} \qquad (5)$$

where $\dot{R}$ represents any reacting radical (for example $\dot{C}H_3$, tri-t-butylphenoxyl, or the peroxide radical), and XOH_0 and XOH_S the reacting molecules of a phenol or alcohol with a free hydroxyl group or with a hydroxyl group solvated by n solvent molecules respectively. This scheme assumes that the radical reacts with the free and solvated molecules with the respective constants k_0 and k_S, and also that solvation equilibrium is established.

With the condition that $k_1 \gg k_0$ and $k_1 \gg k_S$, analysis of scheme (5) leads to the following expression for the rate of disappearance of $\dot{R}$ radicals:

$$-\frac{d[\dot{R}]}{dt} = 2\,\frac{k_0 + k_S K[S]^n}{1 + K[S]^n}[\dot{R}][XOH]_\Sigma,$$

where $[XOH]_\Sigma$ denotes the total concentration of reacting molecules of the phenol or alcohol, and [S] the concentration of solvating molecules. The effective rate constant is given by the expression

$$k_{eff} = \frac{k_0 + k_S K[S]^n}{1 + K[S]^n} \qquad (I)$$

and depends on the concentration [S].

Relationship (I) was analysed for the example of the reaction of tri-t-butylphenoxyl with m-nitrophenol in mixtures of acetone or alcohol as solvating solvents with an inert solvent (heptane)[25]. At low degrees of dilution with heptane, that is with the condition that $K[S]^n \gg 1$, Eqn. (I) can be transformed into

$$k_{eff} = \frac{k_0}{K[S]^n} + k_S. \qquad (II)$$

By differentiating expression (II) with respect to the concentration [S] and taking logarithms, we obtain the equation

$$\log\left|\frac{dk_{eff}}{d[S]}\right| = \log\frac{k_0 n}{K} - (n+1)\log[S]. \qquad (III)$$

From Eqns. (II) and (III) and the experimental dependence of the effective constant k_{eff} on the concentration of solvating solvent [S] it is possible to determine the coordination number n and to calculate the values of k_0/K and k_S.

Fig. 1 shows the dependence of k_{eff} on the concentration of acetone in its mixtures with heptane, and also the logarithmic form of this dependence, which satisfies Eqn. (III). The slope of the straight line *2* gives $n = 1$ and the intercept on the axis of ordinates gives the value $k_0/K = 1.7 \times 10^{-3}$ s^{-1}. From Eqn. (II) we then obtain $k_S = 1 \times 10^{-26}$ cm^3 s^{-1} (at 22°). The coordination number n is also equal to unity for the reaction in methanol.

If the reacting molecule undergoes association not with the molecules of the medium but with other similar molecules, the reaction can again be described by a scheme

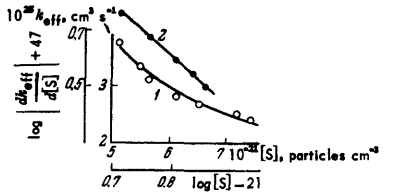


Fig. 1. Dependence of k_{eff} on the concentration of acetone in its mixtures with heptane (curve 1) and its logarithmic transform (straight line 2) [according to Eqn. (III)] for the reaction of m-nitrophenol with tri-t-butylphenoxyl.[25]

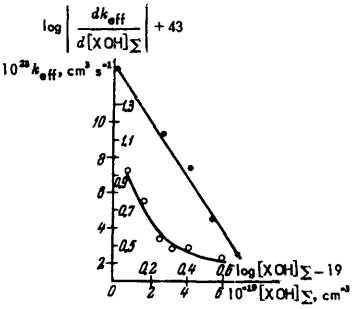


Fig. 2. Dependence of k_{eff} on the concentration of m-nitrophenol and its logarithmic transform [according to Eqn. (IV)] for the reaction of m-nitrophenol with tri-t-butylphenoxyl.[25]

similar to scheme (5), and the corresponding analysis gives the equation

$$\log\left|\frac{dk_{eff}}{d[XOH]_\Sigma}\right| = A + \left(\frac{1}{n} - 2\right)\log[XOH]_\Sigma, \qquad (IV)$$

where A is a constant. From Eqn. (IV) and the data given in Fig. 2 it follows that for the self-association of m-nitrophenol the coordination number $n = 2$.[25]

It should be noted that the coordination number of the solvate complex in the thermodynamic sense denotes the number of solvating molecules present in the complex. The coordination number n appearing in the kinetic equations has its kinetic significance, which does not coincide with the thermodynamic concept. It denotes the number of reactive molecules or groups liberated or held in the elementary equilibrium step of hydrogen bond rupture and formation. Thus in the kinetic equations we cannot use the coordination numbers obtained by physical methods, although in certain particular cases the absolute values of the kinetic and thermodynamic coordination numbers may coincide.

As already noted, in the associates of m-nitrophenol with solvent molecules the value of the kinetic coordination number is unity. This means that only the association of one solvent molecule is significant for kinetics; further association and further growth of the solvate sheath are not significant. In the self-association of m-nitrophenol[25] or diethyl phosphite[19], however, the kinetic coordination number is equal to two, that is two reaction centres take part in the act of complex formation. Thus the reactions of the radicals with the solvated molecules are not elementary reactions, but involve at least three elementary acts: the reaction of the radical with the free non-solvated molecule,

the reaction with the solvate, and the solvation equilibrium. The effective rate constants naturally depend on the concentration of reacting molecules (self-association) or the degree of dilution by an inert solvent (solvation by the solvent). These dependences indicate the existence of specific interactions between the reagents and the molecules of the medium, and they can often be used to investigate the detailed mechanism.

An extremely significant fact in kinetics is that a reaction centre solvated by hydrogen bonding is completely unreactive [18-20] or, strictly speaking, so little reactive that $k_S \ll k_0$. [25]

One reason for this is probably steric hindrance of the reactive group in the solvate. This suggestion alone is obviously insufficient, however, since the distance corresponding to the hydrogen bridge is fairly large and often cannot prevent a reaction by steric hindrance alone. It is clear, for example, that in the reactions of a hydrogen atom, the lack of reactivity of associated hydroxyl groups [23] cannot be attributed entirely to steric effects. Another reason is apparently that the formation of a hydrogen bond in a complex of the type A–H... B leads to partial transfer of charge from the donor B to the acceptor molecule [26] and an increase in the polarity of the reacting bond A–H. This is indicated by the increased intensity of the stretching vibrations of the A–H bond in the infrared spectra, and also by the dipole moments of the complexes and the dielectric properties of substances containing hydrogen bonds [26-29]. The important contribution made by the structure with charge transfer $A^-...H...B^+$ in the complex with hydrogen bonding is also indicated by the linear relationship between the displacement of the stretching and bending vibration frequencies in the hydrogen bridge [30] and by experimental results on NMR chemical shifts on the ^{14}N nucleus of pyridine taking part in hydrogen bonding with methanol [31].

Moreover, there are grounds for assuming that the hydrogen atom in the complex A–H... B is positively charged relative to an ordinary hydrogen atom which is not forming a hydrogen bond, the electron density deficit amounting to 15–20%. This is indicated by electron diffraction data [32], and also by calculation of the NMR chemical shifts (in the one-electron approximation) [33]. It is true that the question of the degree of ionicity of the hydrogen atom is still open [26], but from the kinetic viewpoint the polarisation of the A–H bond in the complex A–H... B is apparently the chief factor leading to the sharp decrease in its reactivity.

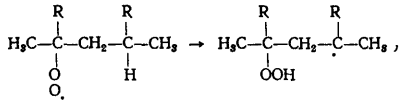
Hydrogen bonding manifests itself not only in the kinetics of radical substitutions, but also in additions across a double bond. Thus *ortho*-substituted *N*-phenylmethacrylamides, whose molecules do not show intermolecular interaction by hydrogen bonding, are polymerised much more rapidly than their *meta*- and *para*-isomers, whose molecules are associated [34].

Until now we have been considering the association of reacting molecules. Let us now consider the influence of association of the radicals on the rate and mechanism of radical reactions. Here two cases are possible: firstly, when the radical forms hydrogen bonds with molecules with which it does not react, and secondly when hydrogen bonding by the radical precedes formation of the activated complex, that is the radical is solvated by the molecule or group with which it reacts. As shown below, the kinetic manifestations of these two possibilities are fundamentally different.

In a study of the decomposition of acetyl peroxide [35] it was shown that the acetyl radicals are more stable in acetic and propionic acids than in aliphatic solvents. This stabilisation of the decomposition of the acetyl radical was attributed to hydrogen bonding between the radical and the acid molecule.

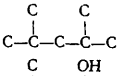
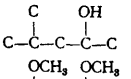
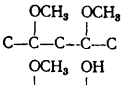
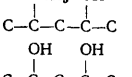
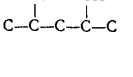
The retarding influence of added water on the oxidation of cyclohexanone was noted by Denisov [36], who showed that this phenomenon is due chiefly to a decrease in the rate constant for chain propagation. This decreased activity of the peroxide radical was assumed to be due to solvation of the radical by water molecules. The proposed kinetic scheme, according to which solvated and non-solvated radicals take part in chain propagation with different rate constants, shows satisfactory agreement with the experimental data. In this paper Denisov formulated clearly for the first time the idea that the participation of radicals in hydrogen bond formation was quite reasonable, and the kinetic consequences of this participation. Subsequent work fully confirmed these ideas.

Thus Rust and Youngman [37], in a study of the oxidation of 2,4-dimethylpentane and 2,4-dimethoxypentane, showed that in these hydrocarbons oxidation proceeds very intensively through intramolecular attack by the peroxide radical on the tertiary C–H bond in the γ-position:

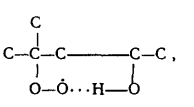


(6)

where R represents a methyl or methoxy group. If one or both of the methyl or methoxy groups are replaced by hydroxyl groups, however, the ability of the hydrocarbons to undergo intramolecular attack by the peroxide radical disappears almost completely. This is effectively illustrated by the scheme given below.

Hydrocarbon	Proportion of products of intramolecular attack, %
	95
	<1
	60–70
	<7.5
	<1

The absence of intramolecular attack (6) in the hydroxyl-containing molecules indicates unambiguously that the peroxide radical forms an intramolecular hydrogen bond of the following type:



which decreases its reactivity with respect to the intramolecular attack at the C–H bond and even leads to a change in the direction of the attack, that is to a change in the oxidation mechanism.

In a number of studies of hydrocarbon oxidation, measurements have been made of the ratios of the constants $k_1/\sqrt{k_2}$ for the reactions of peroxide radicals:

$$\dot{RO}_2 + RH \xrightarrow{k_1} RO_2H + \dot{R}$$
$$\dot{RO}_2 + \dot{RO}_2 \xrightarrow{k_2} O_2 + \text{stable products},$$

in various solvents. It was found that the ratio $k_1/\sqrt{k_2}$ is much smaller in solvents capable of solvating the $\dot{RO}_2$ radical by hydrogen bonding than in inert solvents. This was observed by Howard and Ingold[38] for the oxidation of tetralin and cumene in acetic acid and t-butyl alcohol, by Hendry and Russell[39] for the oxidation of alkenes and arylalkyl hydrocarbons in ethanol and acetic acid, and by Denisov[40] for the oxidation of isopropyl alcohol in methanol and water. These phenomena can be explained on the basis of the theory that the reactivity of the $\dot{RO}_2$ radical is decreased by solvation.

The most convincing proof of solvation of the peroxide radical was obtained by Zaikov and coworkers[41], who measured not only the ratios $k_1/\sqrt{k_2}$, but also the actual constants k_1 and k_2. They showed that solvation of the peroxide radical (in the oxidation of methyl ethyl ketone in aqueous solutions) decreases its reactivity with respect to both chain propagation and disproportionation; the solvate is much less reactive than the free radical, and the coordination number of the solvate is equal to unity. The kinetic data were also used to determine the heat of solvation of the $\dot{RO}_2$ radical.

Walling and coworkers[42-44] studied the competition between two reactions of the t-butoxyl radical — decomposition (7) and substitution (8):

$$(CH_3)_3CO\cdot \xrightarrow{k_{decomp}} (CH_3)_2CO + CH_3\cdot \qquad (7)$$
$$(CH_3)_3CO\cdot + RH \xrightarrow{k_{subst}} (CH_3)_3COH + R\cdot \qquad (8)$$

and the influence of solvents on the quantitative ratio of the products of these reactions. They showed that in a solvating solvent such as acetic acid the difference in the activation energies of reactions (7) and (8), equal to (E_{decomp} - E_{subst}), decreases sharply relative to the value in the gaseous phase or in inert solvents. This effect was attributed to the influence of solvents (and in particular hydrogen bonds) on the activated complex of reaction (7), which is thereby facilitated, with a corresponding decrease in the activation energy E_{decomp}, and hence in the difference (E_{decomp} - E_{subst}). In view of the observation of Levy and Szwarc[35] that the acetyl radical is stabilised by hydrogen bonding, however, it is difficult to suppose that in the present instance hydrogen bonding will facilitate the decomposition of the $(CH_3)_3C\dot{O}$ radical. It appears more probable that hydrogen bonding by the t-butoxyl radical hinders the substitution (8), leading to an increase in E_{subst} and hence to the experimentally observed decrease in the difference (E_{decomp} - E_{subst}). This interpretation explains the results obtained[42-44] and does not contradict the ideas developed by Denisov[36] and confirmed in other work.

The kinetic effects associated with the localised specific interactions between the reacting molecules and radicals and the solvent molecules must apparently be related for the most part not to the activated complex but to the original state, since the lifetime of the activated complex is much less than the characteristic durations of these specific interactions. This remark naturally does not refer to such universal interactions as the dipole–dipole interaction, manifested in the dependence of reaction rates on the dielectric constant of the medium. An example is provided by the detailed work of Zaikov, Maizus, and Emanuel'[45,46] on the influence of the medium on the rate of oxidation of hydrocarbons, alcohols, and ketones, and also by the work of Hendry and Russell[39] on the oxidation of alkenes and arylalkyl hydrocarbons in various solvents.

Thus in all cases when the 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 reaction consists of the ensemble of elementary acts of chain propagation (with the participation of the non-solvated radical and the solvate) and equilibria of radical solvation.

If, however, the radical forms a hydrogen bond with the molecule with which it subsequently reacts, this association facilitates the reaction considerably. Effects of this type were observed by Szwarc and Smid[47] for the decomposition of propionyl and benzoyl peroxides in acetic and trifluoroacetic acids. The ethyl radicals obtained by decomposition of the $C_2H_5C(=O)O\cdot$ radical react with the acids at the C–H or C–F bond. In the decomposition of benzoyl peroxide, the $PhC(=O)O\cdot$ radicals are relatively stable with respect to decomposition and react with the acids at the O–H bond, leading to the formation of $CH_3C(=O)O\cdot$ and $CF_3C(=O)O\cdot$ radicals, which subsequently decompose readily. The final gaseous products were methane and trifluoromethane respectively. Energetically, however, the reaction of the benzoyl radical at the O–H bond in the acid is much less favourable than the reaction at the C–H bond. This anomalous behaviour of the benzoyl radical is due to the characteristic features of its structure, namely its ability to form a hydrogen bond with the hydroxyl hydrogen. This hydrogen bonding precedes the formation of the activated complex and facilitates the reaction.

Analogous effects were observed by Berezin and coworkers[17,18] in a study of the oxidative decarboxylation of acids. In these studies the rate of the reaction of peroxide radicals at the O–H bond in acids was found to be greater by a factor of 13 than the rate of their reaction at the C–H bonds, although energetically the first reaction is less favourable (by almost 12 kcal), so that its rate should have been less than that of the second reaction by a factor of almost 50. Here also, the unusual behaviour of the peroxide radical is apparently due to hydrogen bonding.

Although there are very few papers on the kinetic manifestation of hydrogen bonding involving radicals, there is no doubt that radicals take part in such bonding. Proof for this is provided by the large number of papers on the study of the EPR spectra of radicals in various solvents. It has been shown that the relaxation time and hyperfine splitting in the EPR spectra of radicals depends to a marked extent on the nature of the medium in which the radicals are found[48-52]. This effect is naturally due entirely to the properties of the medium and is regarded by a number of authors[52,54] as a solvation effect. Solvation alters the properties of the unpaired electron, its state, the distribution of its spin density, and hence the reactivity of the radical.

A simple model has been proposed[53] for the solvation of radicals. It was suggested that the changes in the splittings in the spectrum are due entirely to the redistribution of the π-electron spin density of the unpaired electron, and

that this density is influenced by the ligand which is solvating the radical and altering the electronegativity of the atom to which it is attached. Calculations by the molecular orbital method with allowance for the corresponding changes in the Coulomb integrals give the correct sign and magnitude for the observed effects.

Analysis of the EPR spectra of the nitrogen of the stable 2,2,6,6-tetramethylpiperidine *N*-oxide radical[55] showed that in solvating solvents (alcohol, water, or glycerol) the spin density of the unpaired π-electron on the nitrogen atom in the $>\dot{N}-O$ fragment increases by 3–4% relative to its value for inert solvents.

A detailed study of hydrogen bonding with the participation of an unpaired electron was made[56,57] for the example of aliphatic *N*-oxide radicals. It was shown that the changes in the EPR spectra are not related to the dielectric properties of the medium as a whole, but are due chiefly to hydrogen bonding. There is an increase in the constant for the isotropic splitting on the nitrogen as a result of the increase in spin density and possibly a change in bond hybridisation, leading to an increase in the proportion of the *s*-state in the wave function of the unpaired electron. There is a simultaneous decrease in the *g*-factor, the change showing a fairly good correlation with the displacement of the $n-\pi^*$ absorption band of the radical towards shorter wavelengths[58]. Thus the participation of the unpaired electron in hydrogen bonding leads to a significant change in its electronic state.

The same papers[56,57] describe a study of the dynamics of the equilibrium for the solvation of radicals according to the scheme: $R_0 + nS \overset{K}{\rightleftarrows} R_S$, where R_0 and R_S represent respectively "free" radicals and radicals solvated by molecules of the solvent S. The frequency of hydrogen bond formation and rupture was found to be much greater than the difference in the constants for the isotropic hyperfine interaction for the free and solvated radicals, that is the characteristic time required for equilibrium to be established is much less than 2×10^{-7} s. The value of the coordination number *n* for water is equal to unity, and the energies of the hydrogen bonds involving participation of the unpaired electron in the *N*-oxide radicals amount to 4 ± 2 kcal mole^{-1} on the average and do not differ greatly from the energies of ordinary hydrogen bonds. This apparently means that although the state of the unpaired electron in the hydrogen bond does indeed change, the main contribution to the bond energy is made by the donor–acceptor interaction of all the remaining electrons.

Hydrogen bonds involving other radicals, including intra-radical hydrogen bonds, have also been studied[57]. In none of these cases was it possible to obtain hyperfine splitting on the hydrogen atom taking part in hydrogen bonding, because of the short relaxation time for the solvation equilibrium. For strong hydrogen bonds, however, for example in the anion-radicals of naphthazarin and quinizarin[59] this splitting was apparently obtained. Further evidence of this was also provided by data on the scalar paramagnetic relaxation in NMR[60,61], associated with the appearance of an unpaired electron on the hydrogen atom in the hydrogen bridge; the constants for the hyperfine interaction on this hydrogen atom are about 10^4–10^6 s^{-1}. An interesting feature is that the paramagnetic oxygen molecule (triplet ground state) is also solvated by solvent molecules[62].

From the kinetic viewpoint, the formation of a hydrogen bond between the radical and the molecule with which it subsequently reacts may have two effects. Firstly, the formation of this complex may lead to an increase in the entropy of activation of the reaction, since the original state becomes a complex which subsequently undergoes monomolecular decomposition:

$$\dot{R} + HA \rightleftarrows \dot{R}\cdots H-A \rightarrow RH + \dot{A}.$$

Secondly, the participation of the unpaired electron in hydrogen bonding may lead to electronic perturbation of the reacting A–H bond in the complex $\dot{R}\ldots H-A$. Since the unpaired electron is delocalised over the A–H molecule, this complex as a whole can be regarded as a radical; it is possible that exchange or magnetic interactions play an important part in the complex. The idea of these interactions was put forward by McConnell[63] to explain the paramagnetic catalysis of polymerisation and *cis–trans* isomerisation. Berlin and Blyumenfel'd[64] developed this idea to explain the effects of "local activation". These ideas can also apparently be used in radical reactions. Here the reactivity of various radicals and molecules can be explained in terms of exchange interactions in the activated complex, the charge and spin densities at the reactive centre of the radical, etc. At least the kinetic manifestation of hydrogen bonding between radicals and reacting molecules can be readily explained on the basis of these ideas.

3. π-COMPLEXES IN RADICAL REACTIONS

In addition to the influence of hydrogen bonds, another characteristic feature of liquid-phase radical reactions is the influence of the aromaticity of the medium. This has been noted in many papers and is usually attributed to π-complex formation by the molecules and radicals.

According to Mulliken's classification[65], π-complexes are one of the forms of donor–acceptor complexes, in which the donors and acceptors are molecules with labile π-electron clouds (they are also called charge-transfer complexes — CTC). The main interaction in these complexes is between the filled electronic orbitals of the donor and the vacant orbitals of the acceptor.

π-Complexes have now been fairly well studied by physical methods. Electronic transitions between the filled orbitals of the donor and the vacant orbitals of the acceptor in the complex lead to the appearance of new absorption bands in the ultraviolet and visible range, so that spectrophotometry is most widely used to study the structure and properties of these complexes. Not only molecular complexes, but also complexes involving atoms[66–68] and radicals[69–71] have been studied.

The formation of π-complexes, leading to partial transfer of charge within the complex, should alter the electronic structure of the species and their reactivity. This effect should be shown particularly clearly in the kinetics of liquid-phase reactions, in view of the characteristic features of the liquid state.

There are extremely few papers devoted to the kinetic manifestation of π-complexes. We shall examine first π-complex formation by molecules taking part in reactions.

Alder and Leffler[72] observed that the aromaticity of the medium has a marked influence on the decomposition of phenylazotriphenylmethane. The values of the enthalpy and entropy of activation in various solvents were determined with high accuracy and it was shown that there is a linear relationship between them, that is a compensation effect is

observed. Aromatic solvents yield higher values for the enthalpy of activation and higher entropies, the increase in enthalpy on going from cyclohexane to aromatic solvents corresponding approximately to the heats of solvation of the molecules. This suggests that the activation of the decomposition requires preliminary desolvation. Evidence supporting this hypothesis was found by the authors[72] in the parallelism in the changes in the entropies of activation and entropies of fusion of the solvents. If we regard the breakdown of the π-complexes (desolvation) as fusion of the solvate sheath, this parallelism is readily understood. Thus the decomposition of the phenylazotriphenylmethane molecules to form radicals apparently involves consecutive desolvation and decomposition, but the participation of solvates in decomposition is not excluded.

A similar influence of the aromaticity of the medium was also observed in the decomposition of symmetrical diphenylazoethane and bisazomethylpropionitrile[73]. Ziegler did not observe these effects, however, for the decomposition of hexaphenylethane. This is apparently due to steric hindrance and the inability of the phenyl rings of hexaphenylethane to form π-complexes.

Let us now consider π-complex formation by atoms and radicals. Their ability to take part in π-complex formation with a donor is determined by their electrophilic nature (electron affinity) (see Table 2).

The problem of π-complexes involving an $R\dot{O}_2$ radical with a fairly high electron affinity has been very widely discussed for a long time. This discussion was begun in a paper by Boozer and Hammond[74] who put forward a mechanism for the inhibition of oxidation involving a π-complex of the peroxide radical:

$$R\dot{O}_2 + InH \rightleftarrows [RO_2^{\cdot}\cdots InH]$$
$$R\dot{O}_2\cdots InH] + R\dot{O}_2 \rightarrow ROOH + RO_2In.$$

This scheme was subsequently confirmed by Thomas[75] and Denisov[13]. Denisov made a detailed analysis of the conditions under which this mechanism should be revealed kinetically, and showed the limits of its influence.

Zaikov and coworkers[45], Ingold[76], and Russell[39], however, found that the dependence of the rate of oxidation on the dielectric constant of the medium obeys satisfactorily the Kirkwood–Onsager relationship, and no anomalies were observed for the rate of oxidation in aromatic media. Another extremely contradictory paper was published by Thomas[77], in which it was concluded that the $R\dot{O}_2$ radical forms a complex with trialkylamines. Direct experiments using the EPR method to detect π-complexes of the cumene peroxide radicals with a strong donor such as the pyridine molecule did not give positive results: the equilibrium for π-complex formation is displaced considerably towards the free radical[78], whereas even for the iodine molecule (electron affinity only 54.6 kcal mole^{-1}) the complexes with pyridine are extremely stable.

TABLE 2. Electron affinity of various radicals (kcal mole^{-1}).

Radical	Electron affinity	Radical	Electron affinity
$\dot{Cl}$	88.2	$\dot{O}H$	50
$\dot{F}$	83.5	$\dot{C}Rh_3$	48
$\dot{Br}$	81.6	$Ph\dot{O}$	27
$\dot{I}$	74.6	$\dot{C}H_3$	25
$H\dot{O}_2$	70		

Physically, it is extremely difficult to suppose that in the complex $[R\dot{O}_2\ldots InH]$ the interaction involves only π–π interaction and not hydrogen bonding. It might be possible to agree that a π-complex exists if it is assumed that the hydrogen bond between the peroxide radical and the inhibitor molecule InH is fairly weak, but there are as yet no serious grounds for this, rather the reverse: such bonds should be stable[36,37]. Thus at present it is fairly difficult to reach an unambiguous conclusion regarding the existence of π-complexes of $R\dot{O}_2$ with aromatic molecules.

All reactions involving the addition of atoms and radicals to aromatic systems with the formation of σ-complexes do of course involve the formation of intermediate π-complexes. This is apparently the case for the "attachment" of H atoms and $\dot{C}H_3$ radicals to aromatic molecules[79], phenylation[80], hydroxylation[81], and the reactions of peroxide radicals[82]. It is not always possible, however, to detect the intermediate π-complexes as kinetically independent species; this is determined chiefly by the competing reactions of decomposition of the π-complex and its conversion into the σ-complex.

π-Complex formation by the chlorine atom in the chain photochlorination of hydrocarbons has been studied in most detail by Russell[83–85]. In the chlorination of 2,3-dimethylbutane, isobutane, and other branched hydrocarbons the chlorine atom attacks the tertiary C–H bond only four times more readily than the primary bond. In the presence of aromatic solvents this rate ratio increases to 50–300, that is, tremendous selectivity is observed in the reactions of atomic chlorine. The dielectric properties of the medium are of almost no significance, and the order of selectivity (with respect to solvents) shows good correlation with the order of the basic strength of these solvents. This behaviour of the atoms cannot be attributed to the reactions of "hot" atoms and their "cooling" in the aromatic solvents, since the chlorination chains are fairly long, and almost no difference is observed in the rate constants for the gaseous and liquid phases. The most natural assumption is that the Cl atom forms a π-complex with the aromatic molecule and that this complex is much less reactive and hence more selective than the free atom. Analogous effects were observed by Russell[86] in the photochlorination of arylalkyl hydrocarbons.

To explain the regular kinetic features of photochlorination, Russell put forward a scheme involving the reaction of the free Cl atom and its π-complexes with coordination numbers x equal to one and two, and also π-complex formation equilibria between the Cl atoms and one or two aromatic molecules. This scheme does not show sufficiently good agreement with the experimental data[85]. Moreover, it is found that the heat of formation of the complex with x = = 2 is almost 4 times that for the complex with x = 1, which is physically unlikely. Despite the unsatisfactory kinetic analysis, however, there is no doubt that the π-complex is in fact formed and that its selectivity is high.

Berezin and coworkers[87] found that the aromaticity of the medium has a marked influence on hydrogen atom abstraction by the methyl radical from toluene and cyclohexane. The ratio of the rate constants for hydrogen atom abstraction from the aromatic molecule and from cyclohexane decreases sharply with increase in the concentration of benzene or toluene in the mixtures with cyclohexane. This effect at first sight reproduces qualitatively the results obtained by Russell, but it is much more difficult to interpret, since studies were made of the ratio of constants, each of which may depend in different ways on the aromaticity of the medium.

The lack of reactivity in the π-complexes of the t-butoxyl radical in reactions involving the removal of a hydrogen atom can apparently be attributed to the decrease in the ratio k_{subst}/k_{decomp} [see Eqns. (7) and (8)] in aromatic solvents[88-91].

Kinetic data on the influence of aromatic molecules on the rate of recombination of iodine atoms in the gaseous phase were examined by Porter and Smith[92] in terms of complexes with charge transfer between the iodine atoms and the aromatic molecules; the energies of these complexes amount to 1.7–2.4 kcal mole^{-1}. The formation of π-complexes between iodine atoms and hexamethylbenzene in the liquid phase in carbon tetrachloride has been proved spectrophotometrically and kinetically[93]; the equilibrium constant for π-complex formation at room temperature is 2.7 litre mole^{-1}.

A detailed study has been made of the π-complexes of stable aromatic N-oxide radicals and their kinetic manifestation in the removal of a hydrogen atom from 2,6-di--t-butylphenol, which is incapable of undergoing solvation[94]. It was first shown that the rate constants for the reaction of the diphenylnitrogen oxide radical with 2,6-di-t-butylphenol are much smaller in benzene and ethylbenzene than in heptane, the activation energies and pre-exponential terms increasing in the aromatic solvents. Analogous relationships were also observed for substituted diphenylnitrogen oxide radicals.

The kinetic scheme for the reaction of free nitrogen oxide radicals R_0 and their π-complexes R_S with 2,6-di--t-butylphenol PhOH can be represented in general form as follows:

$$\begin{gathered}\dot{R}_0 + PhOH \xrightarrow{k_0} RH + Ph\dot{O} \\ \dot{R}_S + PhOH \xrightarrow{k_S} RH + Ph\dot{O} \\ \dot{R}_0 + nS \underset{}{\overset{K}{\rightleftharpoons}} \dot{R}_S\end{gathered} \qquad (9)$$

where n, the coordination number of the π-complex, shows how many molecules of the solvent S must solvate the radical in order to produce a significant change in its reactivity. The scheme assumes reaction by the free radical and the π-complex, and also π-complex formation equilibrium. Analysis of scheme (9) leads to expression (I) for the effective rate constant k_{eff} for disappearance of the radicals. In an experimental investigation of the dependence of k_{eff} on [S], a study was made of the rate of disappearance of radicals in solvent mixtures, namely in benzene diluted with heptane[94]. The kinetic analysis is here similar to the analysis carried out for hydrogen bonding (see p. 194).

Fig. 3 shows the dependence of k_{eff} on [S] and its transformation into an equation similar to Eqn. (III) for the reaction of dianisylnitrogen oxide with 2,6-di-t-butylphenol at 60°; the value of n obtained from the slope of the straight line is equal to unity. Similar relationships were obtained for various temperatures. The equilibrium constant for π-complex formation by dianisylnitrogen oxide with benzene has the form

$$K = 3.3 \times 10^{-26} \exp(6400 \pm 2000/RT)\ cm^3. \qquad (10)$$

The numerical values of K obtained by the kinetic method show good agreement with the values of K obtained spectrophotometrically[95]; the energy of the bond in the π-complex, determined kinetically, coincides with the bond energy found independently from thermochemical data[96]. This confirms that the kinetic scheme (9) is correct.

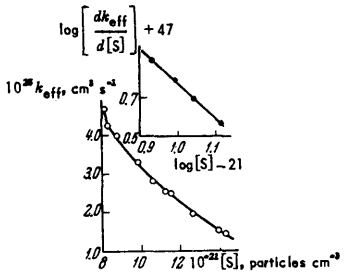


Fig. 3. Dependence of k_{eff} on the concentration of benzene in heptane and its logarithmic transform [according to Eqn. (III)] for the reaction of dianisylnitrogen oxide with di-t--butylphenol.[94]

It is extremely significant that the values of k_S are smaller by an order of magnitude than the values of k_0, that is the π-complex is much less reactive than the free radical; for kinetics, the association of the radical with only one solvent molecule (n = 1) is significant. Further association and further growth of the solvate sheath have no significance, apparently because the first solvating molecule produces the greatest perturbation in the electronic structure of the radical.

The removal of a hydrogen atom from ethylbenzene by various stable N-oxide radicals has been studied[97]. For the reaction of dianisylnitrogen oxide with ethylbenzene, the rate constant increases when the ethylbenzene is diluted with n-decane. This means that the π-complex of the radical with ethylbenzene has a low activity, and no reaction takes place within the complex. This confirms the analogous conclusion reached by Russell[83] for the Cl atom in a π-complex.

The low reactivity of the π-complex is not a general feature. It has been shown[94] that the π-complexes of dianisylnitrogen oxide with pyridine and its derivatives have a high reactivity and react with a smaller activation energy than the free radical. This effect is not due to the influence of the dielectric constant of the medium, since in dichloroethane, whose dielectric constant ϵ is close to that of pyridine, the rate constants and activation energies are almost the same as those in heptane. Thus the reactivity of the π-complex may depend on whether the radical behaves as a donor or an acceptor in the complex.

The problem of whether electron transfer in the π-complex of the radical involves the unpaired electron or includes other lower-lying electrons is of particular interest. Direct measurements, by the NMR method, of the constants for the hyperfine splitting due to delocalisation of the unpaired electron on the molecules of the medium solvating the radical showed that if such delocalisation does in fact take place, it is extremely slight[99]. Studies of the dynamic nuclear polarisation on a number of radicals in aromatic solvents also showed that the degree of delocalisation of the unpaired electron on the ligand in the π-complex is extremely slight[100-102]. There is apparently only slight transfer of charge in the π-complex. The kinetic effects produced by this transfer are fairly large, however.

A compensation effect was observed[97] in the removal of a hydrogen atom from ethylbenzene by aromatic N-oxide radicals. The fact that the radicals for which this effect was observed have extremely similar structures makes it

impossible to attribute the effect to structural differences in the radicals. The origin of the compensation effect must therefore be sought not in the reactivity of the radicals themselves, but in their specific interactions with the medium.

It is apparently a general feature that the compensation effect in liquid-phase radical reactions is usually not observed when the reaction is in fact an elementary reaction. When the reaction is complicated by specific interactions between the reacting species and the solvent molecules (hydrogen bonding, π-complexes), the compensation effect is usually observed. It can be shown that the compensation effect is to be expected when the measured kinetic constants are made up of the rate constants for a number of elementary acts[98].

4. POLAR FACTORS AND SPECIFIC INTERACTIONS IN RADICAL LIQUID-PHASE REACTIONS

As noted above, contradictory experimental facts have been published on the kinetic manifestation of polar factors associated with electrostatic dipole–dipole interactions between the reacting species.

It has been shown in a whole series of papers that the dielectric constant of the solvent has a marked influence on the rate of the radical reactions involved in the oxidation of ethanol and methyl ethyl ketone[45,46,103,104], and alkenes and arylalkyl hydrocarbons[39,76,105], and also the rate of decomposition of t-butyl peroxyformate[106]. In all these examples, the dependence of the reaction rate on the dielectric constant obeys the Kirkwood–Onsager relationship and indicates that the dipolar character of the transition state in these reactions is greater than the dipolar character of the initial reagents.

The dielectric constant of the solvent has absolutely no influence, however, on the rates of the reactions of chlorine atoms with hydrocarbons[85], or of phenoxyl and N-oxide radicals with phenols[24,94], or on the rate of the copolymerisation of styrene with methyl methacrylate or of α-methylstyrene with maleic anhydride[107,108], where it would seem that the strongest polar effects should be revealed. In these examples, as shown above, an important part is played by specific localised interations of the donor–acceptor type.

The latter influence chiefly the initial state of the system, whereas the polar factors exert their chief influence on the activated complex of the reaction. The greater or lesser part played by the polar factors is apparently determined by the electronic structure of the activated complex. The course of the radical reaction $\dot{R} + HX \rightarrow RH + \dot{X}$ can in fact be represented by two schemes:

$$\dot{R} + HX \begin{cases} \xrightarrow{(1)} [\dot{R}\cdots H\cdots X] \rightarrow RH + \dot{X} \\ \xrightarrow{(2)} [R^{(-)}\overset{(+)}{H}X] \rightarrow R^- + H^+ + \dot{X} \rightarrow RH + \dot{X}. \end{cases}$$

Route (1) involves the slow movement of a proton from X to R in the potential field created by rapid electronic motion. Route (2) assumes the transfer of charge from HX to R with the formation of R^- and the cation-radical $\dot{HX}$, which subsequently decomposes to a proton and the radical $\dot{X}$. This reaction path assumes that the charges in the activated complex are separated in time and space; a consequence of this separation is the polarisation of the activated complex and the dependence of the rate on the dielectric constant. The fundamental difference between these routes is that in one case the limiting stage involves the movements of nuclei whereas in the other case electron transfer takes place. Route (2) naturally does not require complete transfer of the electron in the activated complex; only partial transfer, with partial charge separation in the complex, is sufficient.

The realisation of a given form of activated complex depends on the polarity of the medium, which either facilitates the separation of charges or hinders it, and also on the properties of the reacting species — the ionisation potential of the molecule HX and the electron affinity of the radical $\dot{R}$.

This interpretation of the form of the activated complex enables us to look for the possibility of acid–base catalysis of radical reactions. It has in fact been possible to observe examples of both base catalysis (the decomposition of t-butyl peroxyformate in the presence of pyridine)[106] and acid catalysis[109].

Thus the relative part played by polar factors and specific interactions is determined by the form of the activated complex, and its electronic structure.

In conclusion it should be noted that the study of specific localised interactions and polar factors and the part which they play in the kinetics of radical liquid-phase reactions is enriching considerably our knowledge of electronic interactions in the activated complex. The need for further intensive studies in this direction and their undoubted success are obvious.

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THE CHEMISTRY OF HOT HYDROGEN ATOMS WITH 1-3 eV ENERGY AND OF EXCITED RADICALS

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I. INTRODUCTION

Many investigations[1-10] of the chemistry of hot tritium atoms produced by the nuclear reactions $^6Li(n,\alpha)T$ and $^3He(n,p)T$ (recoil energy of the T atoms 2.7 and 0.2 MeV respectively) have shown that these atoms can efficiently take part in chemical reactions when slowed down to energies comparable to those of chemical interaction: in particular, they can take part in transfer and substitution reactions proceeding without activation energy

$$T^* + RH \rightarrow HT + R^\cdot \quad (1)$$
$$T^* + RH \rightarrow RT + H \quad (2)$$

For thermal hydrogen atoms the activation energy of reaction (1) is 9-12 kcal mole^{-1}; reaction (2) is not known to occur with thermal H atoms.

Hot T atoms can add on to the double bond of alkenes, giving excited radicals[6,10], and they can also replace individual atoms or even groups of atoms in complicated molecules[1,7]: when this happens the intermediate products can be used in an excited state, and the decomposition mechanisms will be determined by a number of factors (degree of excitation, efficiency of transfer of the excitation energy, etc.[7,8]).

It should be noted that the formation of fast atoms and of excited molecules and radicals is not confined to processes accompanying nuclear transmutations, but it occurs also in radiolysis, photolysis, and even in thermal reactions at high temperatures.

To explain various anomalies in the behaviour of atoms and radicals, many workers in the field of kinetics have put forward the concept of an abnormally high reactivity for the hot hydrogen atoms and radicals obtained in the radiolysis of hydrocarbons and in the photolytic decomposition of excited molecules.

The majority of workers believe that the primary act in the radiolysis of hydrocarbons is fissure of the C-H bond.

The energy excess $E_{excit} - D_{C-H}$ (where D is the dissociation energy of the C-H bond) apportions itself between R and H in inverse proportion to the masses, and is carried away mainly in the form of kinetic energy by the H atom[11].

Hot H* atoms with a kinetic energy of the order of several electron-volts are reactive at low temperatures as well as at ordinary temperatures[12-14]. Armstrong[14] has demonstrated experimentally the existence of hot hydrogen atoms in his study of the low-temperature radiolysis of HCl at -78° and -196°. These atoms are produced by the decomposition of an excited HCl* molecule ($HCl^+ + e \rightarrow HCl^* \rightarrow H^* + Cl$). Radiation yields G of 4.0 and 2.4 respectively were measured for the formation of hot and of thermal H atoms.

The concept of hot H* atoms has been invoked many times in work on the liquid-phase and gas-phase radiolysis of hydrocarbons[15-17]. Reactions between highly excited H* atoms and C_2H_4 molecules have also been detected mass-spectrometrically[18].

However, a quantitative interpretation of reaction schemes involving hot atoms during radiolysis presents serious difficulties, because of the presence of various competing reactions, of the unknown energy spectrum of the hot atoms, etc.

The most convenient route for the preparation of H* atoms is through photochemical reactions, in particular the photodissociation of the hydrogen halides HI and HBr.

II. FORMATION OF HOT HYDROGEN ATOMS DURING PHOTOLYSIS OF HI AND HBr, AND THEIR REACTIONS

Kondrat'ev and coworkers had shown[19], as long ago as in 1934, that the reactivity of H atoms obtained by the photolysis of HI is essentially dependent on their kinetic energy.

Hydrogen iodide has a continuous absorption spectrum in the ultraviolet region, beginning at 3850 Å.[20,21] The maximum extinction coefficient ϵ lies in the region of 2500 Å, and has a value of $\sim 2 \times 10^{-19}$ cm^2 per molecule[20]. Since ϵ_{HI} is high in the region of 2500 Å, and most of the radiation with λ = 2537 Å is absorbed in the first centimeter of optical path at atmospheric pressure, the experiments are usually made at lower HI pressures (~ 10-30 mmHg).

The most commonly used sources of ultraviolet radiation are low-pressure cadmium or mercury resonance lamps of type Hanovia SC 2537 (or lamps type PRK-2 or PKR-4, made in the Soviet Union). For experiments at λ = 1849 Å these lamps are fitted with a Suprasil window[22,23], and with a filter of lithium fluoride irradiated with X-rays or γ-rays,