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Kinetics and Mechanism of the Reaction of Peroxy-compounds with Phosphites, Sulphides, and Aromatic Amines

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The studies dealing with the elucidation of the detailed mechanism and quantitative kinetics of the reactions of peroxy-compounds with phosphites, sulphides, and aromatic amines are reviewed. It is shown how evidence has been obtained by ESR of the existence of the one-electron amine oxidation stage, i.e. the stage involving the formation of radical-cations. The consecutive reactions of the radical-cations formed initially and their relation to the behaviour of the amines as polymerisation initiators are analysed. The characteristics of the detection of free radicals in reactions of phosphites and sulphides with hydroperoxides are examined and certain criteria of the latent radical nature of these reactions are formulated. In the last section correlations of the Hammett equation type for rates of the reactions under consideration and also the correlation between the rate constants on the one hand and the ionisation potentials and electron affinities on the other are discussed within the framework of the one-electron oxidation-reduction mechanism. The bibliography includes 96 references.

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I. INTRODUCTION

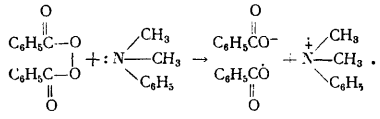
The reduction of peroxy-compounds by phosphites, sulphides, and aromatic amines constitutes a large and important class of organic reactions. On the basis of N. M. Semenov's hypothesis concerning the possibility of the formation of free radicals in the bimolecular interaction between valence-saturated molecules, one may also expect the formation of radicals in the above reactions. This assumption follows from the fact that, since one of the reactants (the peroxide) is a powerful oxidising agent and the other is a powerful reducing agent, the reaction does not require a large activation energy (10–20 kcal mole^{-1}). However, one cannot exclude the possibility that another mechanism, which does not lead to the formation of free radicals, is even more effective. There is no unanimous view in the literature concerning the mechanism of the reactions of peroxy-compounds with amines, phosphites, and sulphides; therefore, it is necessary to make a critical analysis of the results available in this field and their interpretation.

Moreover, there is also a purely practical aspect of the investigation of these reactions associated with the behaviour of aromatic amines as initiators of the radical polymerisation of monomers, phosphites, and sulphides and as synergists in polymer stabilisation processes.

II. KINETICS AND MECHANISM OF REACTIONS OF AROMATIC AMINES

The chemistry of the interaction of aromatic amines with peroxy-compounds, particularly with benzoyl peroxide[1-6], has been investigated in greatest detail. Gambaryan[1] established that primary, secondary, and tertiary aromatic amines rapidly react with benzoyl peroxide (BP) with formation of benzoic acid and *O*-benzoylhydroxylamine or its *N*-alkyl derivatives.

According to Horner's hypthesis[2,3], the first stage for all amines is the formation of a complex of the amine and benzoyl peroxide in which an electron is transferred from the lone pair of the amine to the peroxide molecule, involving the formation of an ion pair and a benzoate radical. For example, for dimethylaniline (DMA) (a tertiary amine), we have



The second stage consists in proton transfer from the methyl group or the benzene ring of the amine radical-cation to the benzoate anion; this is accompanied by the formation of a radical pair, which enters into further reactions leading to the formation of the final products. The appearance of an intense colour when dimethylaniline reacts with benzoyl peroxide in chloroform in the presence of chloride ions is regarded by Horner and Schwenk[2] as evidence of the formation of the dimethylaniline radical-cation.

Dimethylaniline radicals were first obtained by the irradiation of the initial amines with light[7] at a wavelength of 2700 Å or by flash photolysis[8] and were investigated spectophotometrically[7,8]. The absorption spectrum of the radical-cations in aqueous and EPA (ether : isopentane : ethanol = 5 : 5 : 2) solutions is characterised by a broad band with a maximum at 4600 Å.

The appearance of a band with a more diffuse maximum at 4600–4700 Å was observed by Stavrova et al.[9] in the reaction between benzoyl peroxide and dimethylaniline in EPA at 20°C; they attributed this band to the dimethylaniline radical-cation formed as a primary species. Indeed, this result is without any doubt evidence of the formation of amine radical-cations in the benzoyl peroxide–dimethylaniline system. However, the problem arises whether these radical-cations are primary or secondary species. Spectrophotometry cannot provide an unambiguous and reliable answer; electron spin resonance (ESR) is likely to be the most suitable method.

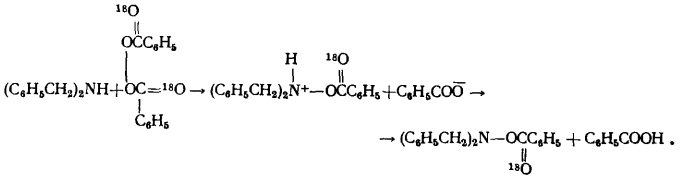
The formation of neutral free radicals in the reaction of benzoyl peroxide with dimethylaniline and other tertiary amines was observed directly in a number of studies. Horner[2] showed that the benzoyl peroxide–dimethylaniline system is capable of initiating the radical polymerisation of various vinyl compounds at 20°C, the initiating agent being the benzoate radical. An analogous initiation effect in the polymerisation of styrene was also observed following the addition of *p*-dimethyltoluidine to benzoyl peroxide[10]. Imoto et al.[11] determined the effectiveness of the initiation at 25°C of the polymerisation of styrene by the benzoyl peroxide–dimethylaniline system. They compared the rate of initiation calculated from the rate of polymerisation and the values of $k_p/k_t^{1/2}$ with the rates of reaction of benzoyl peroxide and dimethylaniline; the effectiveness of the initiation proved to be 0.25. Hrabák[5,12] showed that the rate of reaction of dimethylaniline, methyltolyltoluidine, and tritolylamine with benzoyl peroxide in benzene solution decreased severalfold in the presence of the stable diphenylpicrylhydrazyl (DPPH) radicals or nitric oxide; the replacement of benzene by other solvents also led to retardation of the reaction. The results can be explained by the fact that the radicals arising in the bimolecular reaction of benzoyl peroxide with tertiary amines (HA) initiate the chain reaction according to the mechanism

$$C_6H_5COO\dot{} + HA \rightarrow C_6H_5COOH + \dot{A}\,, \qquad (1)$$

$$\dot{A} + (C_6H_5COO)_2 \rightarrow C_6H_5COO^{\cdot} + C_6H_5COOA\,. \qquad (2)$$

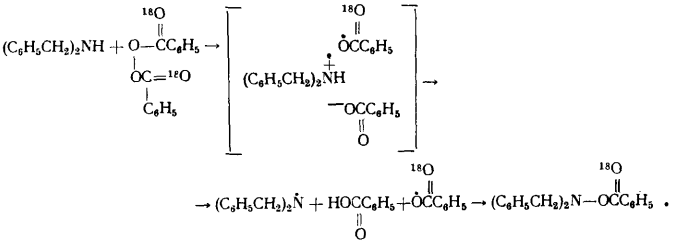
The kinetics of the reaction of benzoyl peroxide with dimethylaniline were studied by many investigators[6,10-15], all of whom established that the rate is proportional to the concentration of amine and peroxide in accordance with a bimolecular mechanism of the initial stage of the process. In one of the papers[6] the activation energy for this reaction is quoted as 14.8 kcal mole^{-1}; according to another[17], it is 12.8 kcal mole^{-1}. As regards the initiation of polymerisation as a method for the quantitative determination of radicals, the studies on different monomers[14-17] yielded for the rate of polymerisation w_n a relation of the type $w_n = k[DMA]^{1/2}[BP]^{1/2}$ corresponding to a bimolecular formation of benzoate radicals. Since the reaction between benzoyl peroxide and dimethylaniline is of the chain type, the experimentally observed second order can be accounted for only by cross termination by benzoate and amine (A) radicals.

Donald and Dorothy Denny[18] investigated the mechanism of the reaction of secondary amines with benzoyl peroxide using isotope tracers. Thus, when benzoyl peroxide, the carbonyl oxygen of which contained 1.32 at.% ^{18}O, was allowed to react with dibenzylamine, *O*-benzoyl-*NN*-dibenzylhydroxylamine was isolated in 57% yield as the product. Chemical determination of ^{18}O showed that the same amount of the isotope is retained in the carbonyl groups of both *O*-benzoyl-*NN*-dibenzylhydroxylamine itself and the product of its solvolysis by sodium ethoxide—(ethyl benzoate). On the basis of these results, a mechanism was proposed, as an alternative to that of Horner, involving a nucleophilic attack by the amine on the peroxy-bond with formation of an ion pair, which is converted into the reaction products via proton transfer:



A similar mechanism is suggested also for the reactions of primary amines[18].

It is noteworthy that the distribution of oxygen-18 in the reaction products may be explained within the framework of the one-electron transfer hypothesis:



Moreover, many facts are contrary to the concept of a nucleophilic mechanism. For example, secondary and primary amines initiate at 25°C the polymerisation of monomers[20,21], although with a low effectiveness; thus the effectiveness for diphenylamine (DPA) [20] is about 10^{-3}. The absorption of nitric oxide by the reacting benzoyl peroxide–diphenylamine system[22] indicates the intermediate formation of free radicals. Bagdasar'yan and Milyutinskaya[20] showed that these radicals are capable of reacting with diphenylpicrylhydrazine (DPPH-H), which is then oxidised to DPPH radicals. Finally, free radicals were detected[23] by ESR following the mixing of benzene solutions of benzoyl peroxide and aniline or its *p*-methyl and *p*-ethyl derivatives (at 20°C); in all cases these proved to be diphenyl(diaryl)nitroxide radicals.

The hyperfine coupling (HFC) constants for the ^{14}N nuclei and the protons of the aromatic ring and the g-factors for these radicals (2.0059) agree well with the above interpretation of the ESR spectra.

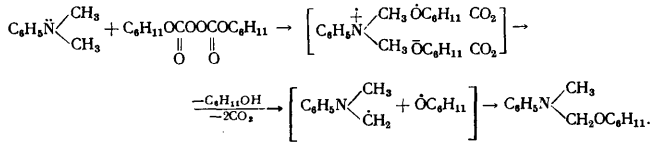
However, direct evidence of the formation of radical-cations derived from the secondary or primary amines (according to Horner's mechanism) is not given in any of the studies quoted above; moreover, all the facts confirming the radical mechanism of the reaction of these amines with benzoyl peroxide are frequently associated with secondary radical products.

The reaction of benzoyl peroxide with aniline, diphenylamine, and secondary aliphatic amines is of the second order (according to the initial rates) and has low activation energies: 16.4 kcal mole^{-1} for diphenylamine[20], 10.7 kcal mole^{-1} for aniline[20], 10.5 kcal mole^{-1} for diethylamine[22], and 14.8 kcal mole^{-1} for di-n-butylamine[22]. Since the reaction of benzoyl peroxide with tertiary amines, for example dimethylaniline, has a chain mechanism, the problem arises whether the mechanism of its reactions with secondary and primary amines is also of the same type. It was shown[20] that the addition of DPPH-H does not affect the rate of reactions of benzoyl peroxide with diphenylamine, although DPPH-H is then converted into DPPH. If this reaction were of the chain type, its rate would decrease in consequence of the formation of the inactive DPPH radicals, incapable of propagating the chain reaction. The absence of an inhibiting effect on addition of isoprene to the benzoyl peroxide–aniline system also indicates that this reaction has a non-chain mechanism. The absence of an isotope effect on replacement in aniline and diphenylamine molecules of a hydrogen atom by deuterium is also contrary to the hypothesis of a chain mechanism for the reaction since in a chain reaction the rate constant ratio k_D/k_H for stage (1) would not be unity. Thus, although the reactions of aniline and diphenylamine with benzoyl peroxide do in fact lead to the formation of free radicals, they are not of chain type.

It is not clear which stage determines the rate of reaction of secondary and primary amines with benzoyl peroxide. The absence of an isotope effect in the reaction of the *N*-deuterated compound[20] is evidence that the transfer of a hydrogen atom or proton from the amine to benzoyl peroxide is not the rate-determining state of the process and it may be that the rate is in fact determined by the transfer of an electron from the amine to the peroxide.

Comparatively little is known about the formation of radicals in the reaction of amines with peroxides of another type—peroxydicarbonates. A striking example illustrating the possibility, in principle, of the formation of radicals in this system is the observation by Vasil'ev and Nalbandyan[24] of chemiluminescence in the visible part of the spectrum arising from interaction between dimethylaniline and dicyclohexyl peroxydicarbonate (CPC) at 20°C in benzene. It was shown that, in the absence of oxygen, the chemiluminescence intensity I is a maximum at the instant of mixing of the reactants and decreases according to the law $I^{-1/2} = I_0^{-1/2} + dt$, which can be readily derived on the hypothesis that the excited product is formed via a bimolecular reaction between dimethylaniline and dicyclohexyl peroxydicarbonate.

Razuvaev et al.[25] analysed the products of this reaction and isolated 1.97 moles of CO_2, 0.88 mole of cyclohexanol, and 0.8 mole of *N*-cyclohexyloxylmethyl-*N*-methylaniline per mole of decomposed dicyclohexyl peroxydicarbonate. On the basis of the composition of the products, a reaction mechanism, analogous to Horner's mechanism for benzoyl peroxide, was proposed:



Since the reaction product is a highly luminescent amine derivative, one may suppose that this compound, formed by radical recombination, in fact serves as the chemiluminescence emitter.

The energy relations of this reaction have not been investigated at all. It is only known that the reaction of di-isopropyl peroxydicarbonate with methyldiphenylamine is described by an Arrhenius temperature equation of the type

$$k = 10^{11} \exp(-19\,400/RT) \text{ litre mole}^{-1}\text{ s}^{-1}.$$ [26]

The oxidation of aromatic amines by organic peracids, which yields amine oxides (in the case of tertiary amines) or phenylhydroxylamines and nitroso-, nitro-, azo-, and azoxy-compounds (in the case of primary and secondary amines), has been for a long time a well known synthetic reaction (its chemistry was described in detail in other reviews[27,28]).

The results of the kinetic analysis of these reactions [second kinetic order, low activation energies (about 13 kcal mole^{-1}) and the absence of an effect of methyl methacrylate (MMA) on the rate] can be accounted for by a nucleophilic mechanism[27,29].

Rassat and coworkers[30] investigated by ESR the intermediate products in the oxidation of a large class of primary, secondary, and tertiary aromatic and heterocyclic amines by *p*-nitro- and *m*-chloro-perbenzoic acids in various solvents: in all cases these proved to be nitroxide radicals. However, the pathways in the formation of these radicals are obscure; it is only clear that they are secondary products derived from the amines. Thus it is at present difficult to arrive at an unambiguous conclusion concerning the applicability of the radical mechanism to the oxidation of amines by peracids solely on the basis of the detection of nitroxide radicals, although this mechanism is not inconsistent with the results of kinetic analysis.

Hydroperoxides also react readily with amines and are at the same time reduced into the corresponding alcohols in fairly high yields (72–100%)[31]. The composition of the amine oxidation products is complex and depends on the nature of the amine[32].

The reactions of cumenyl peroxide with phenothiazine, its 3,3-dimethoxy-derivative, and diphenylamine have been investigated by ESR[33] in deoxygenated (to a residual pressure of 10^{-2} mmHg) benzene solutions between 20° and 160°C. The formation of nitrogen radicals derived from phenothiazine and its derivative was observed even at room temperature. When the thioamine was taken in an excess (100:1 or 10:1) there were no changes in the ESR spectra of these "primary" radicals even on heating to 60–70°C. In the presence of an excess of the hydroperoxide and at 60–70°C the "primary" nitrogen radicals were gradually converted into the "secondary" nitroxide radicals, probably via the mechanism

$$Ar_2\dot{N} + R'OOH \rightarrow Ar_2N{-}OH + R'\dot{O}\,, \qquad (3)$$

$$Ar_2N{-}OH + R'OOH \rightarrow Ar_2N{-}\dot{O} + H_2O + R'\dot{O}\,. \qquad (4)$$

The ESR spectra of the "primary" and "secondary" thioamine radicals differ significantly in the splitting (a_N^{sec} is greater by about 30% than a_N^{prim}), in the nature of the hyperfine structure (HFS), and in the values of the *g*-factors ($g^{prim} = 2.0029$ and $g^{sec} = 2.0038$). With diphenylamine, the nitroxide radicals are detected immediately.

The formation of nitroxide radicals in 100% yield was also observed by Coppinger and Swalen[34] using ESR in the oxidation of a large class of secondary and tertiary aliphatic and secondary aromatic amines by *t*-butyl hydroperoxide (TBHP). These results convincingly demonstrate that nitroxide radicals are formed in all cases according to the mechanism represented by reactions (3) and (4).

The mechanism of the primary elementary steps in the interaction of hydroperoxides with amines remains obscure. It has been suggested that[33] nitrogen radicals are formed from amines by a molecular mechanism:

$$Ar_2NH + R'OOH \rightarrow Ar_2\dot{N} + H_2O + R'\dot{O}\,.$$

A similar mechanism was considered, for substituted hydrazines alone, also by Maruyama et al.[35] When t-butyl hydroperoxide was allowed to react with DPPH-H in benzene at 60°C, they detected and identified by hydrazyls radicals, by comparing the hyperfine structure and the overall width of their ESR spectrum with that of a standard—DPPH radicals. Triphenylhydrazine was oxidised under milder conditions (4°C) and the reaction was accompanied by the successive appearance of three types of ESR spectra, which were attributed respectively to the radicals Ph_2-NPh, PhN-OH, and Ph_2NO. However, the interpretation of the ESR spectra of the first two radicals gives rise to doubts and consequently the assignment of the spectra to the above products cannot be regarded as unambiguous.

The kinetics of the reactions of hydroperoxides with amines have been investigated in a number of studies. It was shown that the rates of these reactions are

described by second-order kinetic equations; the results of the kinetic analysis are presented in Table 1.

It follows from the analysis of the literature data that the formal kinetics of the reactions of peroxy-compounds with aromatic amines and the composition of the reaction products have been fairly adequately investigated; there is a need for a revision of only the fundamental aspect of the mechanism—the detection and identification of the primary radical-cations derived from the amines and the interpretation of the reactions of the radicals.

Table 1. Pre-exponential factors and the activation energies for the reactions of amines with hydroperoxides.

Amine	Hydroperoxide	Solvent	k_0, litre, mole^{-1} s^{-1}	E_{act}, kcal mole^{-1}	Refs.
Diethylamine	cumenyl hydroperoxide	Water	$8.7 \cdot 10^9$	17.0	36
Triethylamine	cumenyl hydroperoxide	Water	$5.4 \cdot 10^8$	14.7	37
Pyridine	t-butyl hydroperoxide	Chloro-benzene	$1.9 \cdot 10^7$	21.0	38
Triphenylhydrazine	t-butyl hydroperoxide	Benzene	$0.2 \cdot 10^2$	5.6	35*
N-cyclohexyl-*N'*-phenyl-*P*-phenylene-diamine	polypropylene hydroperoxide	Solid phase	$1.3 \cdot 10^5$	13.0	39

* The values of k_0 and E_{act} were determined by the present authors from the data of Maruyama et al.[35]

The results of experiments[40-42] unambiguously confirm the existence of a one-electron amine oxidation stage, i.e. the stage involving the formation of radical-cations; this is clearly confirmed by the observation of the ESR spectra of the radical-cations of dimethylaniline, *NNN'N'*-tetramethyl-*p*-phenylenediamine, 2,2',4,4',6,6'-hexamethoxydiphenylamine, *p*-phenylenediamine, and *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine formed in the reactions with various peroxy-compounds: benzoyl peroxide, dicyclohexyl peroxydicarbonate, t-butyl hydroperoxide, and olefin ozonides†. The isotropic and anisotropic hyperfine coupling constants for the ^{14}N nuclei and protons of the amino-groups and aromatic rings and also the unpaired electron densities were determined.

For example, the radical-cation derived from dimethylaniline gives rise to an ESR spectrum with a complex hyperfine structure due to the coupling of the unpaired electron with the nitrogen nucleus (a_N = 10.0 Oe), the protons of the methyl groups ($a_{H(NCH_3)}$ = 11.8 Oe), and the *ortho*- (a_H^o = 1.7 Oe), *meta*- (a_H^m = 0.8), and *para*-protons (a_H^p = 5.2 Oe) of the aromatic ring.

It is noteworthy that the observed constant a_N is in good agreement with data[43-45] for the radical-cations derived from *para*-substituted dimethylanilines formed on oxidation of the amines by Ce^{4+} ions in a flow system[43] or electrochemically[44,45]. Table 2 lists the hyperfine coupling constants for the ^{14}N nucleii of the radical-cations of dimethylaniline and its *para*-derivatives (in oersteds); evidently the constants a_N are correlated with Hammett's σ parameters, the relation being linear (Fig. 1).

† The reaction of amines with ozonides had not been reported previously.

Subsequently the electronic structure of the dimethylaniline radical-cation was calculated[45] by the Hückel molecular orbital method. The Coulombic and exchange integrals for the nitrogen atoms were assumed to be given by expressions of the form $\alpha_N = \alpha_C + 0.50\beta_{CC}$ and $\beta_{CN} = \beta_{CC}$. The calculated unpaired electron density at the nitrogen atom ρ_π^N proved to be 0.5181. Using this theoretical value of ρ_π^N, the a_N constant for the dimethylaniline radical-cation can be estimated with the aid of the familiar relation $a_N = Q_N \rho_\pi^N$ (where Q_N = 20.6 Oe).[46] The result is a_N = 10.7 Oe, which is very close to the experimental value in Table 2.

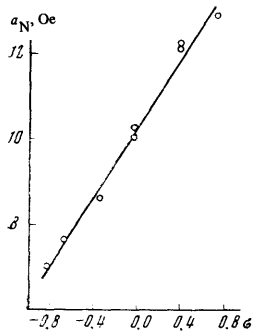


Figure 1. a_N/σ diagram for the hyperfine coupling constant of the radical-cations of dimethylaniline and its *para*-derivatives.

Table 2. The values of a_N (in oersteds) for the radical-cations of dimethylaniline and its *para*-derivatives.

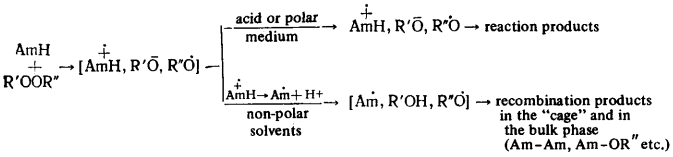
Compound	a_N, Oe	δ_{para}	References
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—$N(CH_3)_2$	6.99	−0.83	44
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—NH_2	7.62	−0.66	45
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—OH	8.6	−0.32	43
$(CH_3)_2\dot{N}^+$—C$_6$H$_5$	10.0	0.0	43, 44
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—$NHCOCH_3$	10.24	0.0	45
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—CHO	12.1	0.45	45
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—$COOC_2H_5$	12.14	0.45	45
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—NO_2	12.8	0.78	45

In the ESR spectrum of the radical cation of another amine (2,2',4,4',6,6'-hexamethoxydiphenylamine) there are four lines with intensity ratios close to 1 : 2 : 2 : 1, due to the coupling of the unpaired electron with the ^{14}N nucleus and the NH proton, which are approximately equivalent (a_N = 7.5 Oe and $a_{H(NH)}$ = 8.1 Oe). This radical-cation is very stable: it is clearly detected over a period of several days and in acid media its yield is close to 10%.

The radical-cations derived from amines have been investigated in various solvents. In non-polar solvents the radical-cations are usually unstable and undergo secondary reactions. The sequence of these reactions is well illustrated by the following example.

The radical-cation is deprotonated to give a nitrogen radical. The ESR spectrum of the latter is a 1 : 1 : 1 triplet due to the coupling of the unpaired electron with the nitrogen nucleus (a_N = 8.1 Oe). These nitrogen radicals then recombine to give hydrazine. As a result of a secondary electron transfer from hydrazine to the peroxide or the primary radical-cation, a secondary hydrazine radical-cation is produced. Its ESR spectrum at 20°C and at 77°K consist of five lines due to the coupling of the unpaired electron with the two equivalent nitrogen nuclei. The isotropic hyperfine coupling constant for this radical-cation is 6.6 Oe, the anisotropic coupling constant is 5.2 Oe, and the unpaired electron density at each nitrogen atom is 0.41. [41]

Analysis of the structures of the radical-cations and their reactions enabled the authors [40,41] to propose the following general mechanism for the reaction of peroxy-compounds with aromatic amines:



The mechanism includes electron transfer from the amine to the peroxide and the formation of an ion-radical pair. In acid and polar media the radical-cations are stabilised. In non-polar solvents the radical-cations are deprotonated to give radical products.

The effectiveness of the initiation of polymerisation by the amine–peroxide system may be accounted for by this mechanism: it is determined by the relative probabilities of the release of an individual radical into the bulk phase and of the transfer of a proton from the radical-cation to the anion with subsequent recombination of the radical pair within the cage.

Thus the detection by ESR of the radical-cations of various aromatic amines [40-42] unambiguously proves the validity of the hypothesis that electron transfer is the first stage of the reaction of amines with various peroxy-compounds: diacyl peroxides, peroxydicarbonates, hydroperoxides, and olefin ozonides. This means that the mechanism of the one-electron oxidation of aromatic amines is probably common to all classes of peroxy-compounds; previously direct evidence had not been obtained for this conclusion. One may suppose that this mechanism is probably valid also for aliphatic amines.

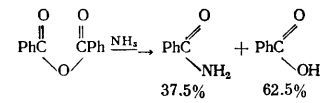
III. KINETICS AND MECHANISM OF REACTIONS OF PHOSPHITES

Whereas the reactions of the majority of peroxy-compounds with amines have been fairly well investigated and there is no doubt that they involve the formation of free radicals, the study of the reactions of peroxy-compounds with phosphites having the general formula $(RO)_3P$ (where R = alkyl or aryl) was until recently restricted solely to stereochemical and isotopic investigations which do not allow unambiguous and reliable conclusions concerning the mechanism of these reactions; moreover, the conclusions concerning the nature of the reactions were frequently made, as will be shown below, on the basis of an analysis of the reactions of phosphite analogues—phosphines R_3P.

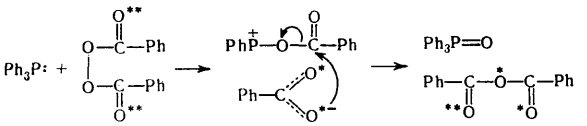
Under mild conditions (at 0°C and below), peroxy-compounds react with phosphines and phosphites to form the corresponding derivatives containing the phosphoryl group P=O (the chemistry of these reactions was described in detail in other reviews [47-51]). The reactions take place with a large heat change (the P=O bond energies are in the range 120–150 kcal mole^{-1} [47,52]). The reactions are also promoted by the easier polarisability of the phosphorus atom compared with the nitrogen atom and possibly $d_\pi - p_\pi$ conjugation, which lowers the energy of the transition state.

Denney and coworkers [53] investigated the mechanism of the reaction of benzoyl peroxide with triphenylphosphine by the isotope tracer method: one of the reactants (benzoyl peroxide) contained ^{18}O in the carbonyl group. It was established that the heavy isotope is fully transferred to only one final product—benzoic anhydride (in the other product, phosphine oxide, there is no ^{18}O). This implies that carbonyl oxygen is not involved in the reaction.

The distribution of ^{18}O in the anhydride was determined by reaction with liquid ammonia. It was found that 37.5% of heavy oxygen is contained in benzamide:



The authors believe that such distribution is possible only when the phosphine attacks the peroxy-oxygen with formation of an ion pair; the latter is converted into the final reaction products by S_N2 nucleophilic substitution:



(* = 1 conventional ^{18}O unit)

An ionic mechanism is also postulated for the reaction of benzoyl peroxide with triallyl phosphite [51] but only on the basis of the usual analysis of the final products (phosphate and anhydride).

However, as in the case of amines, the distribution of ^{18}O in the products of the reaction of benzoyl peroxide with phosphines may be accounted for by the hypothesis of electron transfer as the first stage of the reaction, the isotope tracer method establishing unambiguously only that there is no exchange of carbonyl oxygen atoms without providing more detailed information about the nature of the primary elementary steps of the reactions of peroxides with phosphines and hence also with phosphites.

Among the reactions of phosphites with other peroxy-compounds, those with hydroperoxides are important; the most significant advance achieved is that the mechanism of the elementary stages of these reactions has now been elucidated quantitatively. The first study was published in 1959. Walling and Rabinowitz [54] established that trialkyl phosphites decompose hydroperoxides to a trialkyl phosphate and an alcohol. They suggest that the ion-pair $[(RO_3\overset{+}{P}-OR', {}^-OH]$ is formed as an intermediate. However, Denney et al. [55] believe that the formation of an ion pair of a different structure, $[(RO)_3\overset{+}{P}-OH, {}^-OR']$, converted into the products (phosphate and alcohol) by proton transfer, is more likely. This last hypothesis is based

on the fact that, in the first place, the reduction of hydroperoxides by phosphines in ethanol–$H_2{}^{18}O$ solution yields a phosphine oxide and an alcohol, both without ^{18}O, which can be accounted for by the absence of free OH^- ions and their isotope exchange with the solvent $^{18}OH^-$ ions and, in the second place, by the fact that the optical activity of the initial hydroperoxide is retained in the alcohol formed[56].

However, these arguments put forward by Denney in favour of a nucleophilic mechanism can also be accommodated within the framework of the one-electron mechanism.

Isotope exchange with $^{18}OH^-$ is non-obligatory because the radical–ion pair $[(RO)_3\dot{P}^+, R'O\bar{O}H]$ can be converted by a monomolecular mechanism into the radical pair $[(RO)_3\dot{P}-OH, R'\dot{O}]$.

Furthermore, the optical activity is retained not only in the $R'O^-$ anions but also in the $R'\dot{O}$ radicals. Thus, in the pyrolysis of the laevorotatory t-butyl α-phenylethyl peroxide in thiophenol, α-phenylethanol is formed[57], i.e. the optical activity does not disappear from the alkoxy-radical‡.

Bearing in mind the unsatisfactory evidence for the mechanism put forward, Denney himself questions it and suggests another mechanism for the initial stage, including the migration of a hydrogen atom in a three-centre activated complex $[R'-\underset{H}{O}\cdots O-P(OR)_3]$. However, this pathway is also unlikely, since it presupposes the dissociation of two bonds simultaneously in a single activated complex. The process most probably consists of a consecutive series of elementary dissociation steps via the intermediate formation of the radicals $R'O$ and $HO\dot{P}(OR)_3$.

On this hypothesis, it was shown[40,59,60] that the introduction of stable iminoxy-radicals, which are powerful free radical acceptors[61], into hydroperoxide–aliphatic phosphite [triethyl phosphite (TEP), tripropyl phosphite (TPP), and iso-octyl diphenyl phosphite] systems leads to their destruction§. This implies that free radicals are formed in the reaction between hydroperoxides and phosphites. The yield of free radicals in the reaction was measured and found to be of the order of 10^{-4}. Direct experiments designed to detect by ESR the free radicals derived from aliphatic phosphites were unsuccessful, probably because of the high rate of destruction of the radicals and their correspondingly low steady-state concentration.

Since the elementary step involving the destruction of radicals is exothermic, the appearance of chemiluminescence in the test system was to be expected; moreover, the energy liberated as a result of these reactions is sufficient for the electronic excitation of their final products [for example, the heat of reaction of triethyl phosphite with t-butyl hydroperoxide, which we estimated as the difference between the heats of formation of the final products (phosphate and alcohol) and the initial reactants, proved to be about 116 kcal mole^{-1}; the values of ΔH_f° for the phosphite and phosphate taken from the literature[62,63] were employed in the calculations].

‡ Recently Bentrude[58] established that the transfer of an oxygen atom from the $R'\dot{O}$ radicals to the optically active phosphines $R_1R_2R_3P$ takes place with retention of the configuration, i.e. the optical activity also does not disappear from the phosphoranyl radical $R_1R_2R_3\dot{P}-OR'$.

§ The experiment designed to investigate the kinetics of the destruction of the acceptor (at 20°C in benzene) was performed on an EPR-2 IKhF spectrometer.

Indeed a luminescence was observed[40,64] in the reaction of t-butyl hydroperoxide with triethyl phosphite and tripropyl phosphite in benzene at 20°C in the absence of oxygen. It was found that the luminescence intensity and the reaction rate constant did not change in the presence of stable iminoxy-radicals; the acceptor was employed at concentrations which were the same as those in the experiments where it was shown by ESR[59] that it captures completely all the radicals released into the bulk phase. This result is important; it implies that the excitation step is not influenced by additional active components of the chemical system, i.e. the emitter (this proved to be the triplet molecule of the reaction product—phosphate[64]) appears in the exothermic step involving the destruction of the free radicals $R'\dot{O}$ and $HO\dot{P}(OR)_3$, which does not take place in the bulk phase but in the "cage" where they are formed.

Thus the chemiluminescence observed in the reaction of t-butyl hydroperoxide with phosphites is a source of information about the processes within the cage.

The question arises of the causes of the low number of radicals released from the cage into the bulk phase (about 10^{-4} of the number of hydroperoxide molecules which have reacted). One of these is probably the small distances between the radicals in the cage.

The cage effect is known[65] to depend strongly on the "diameter" of the cage, i.e. on the distance r_0 between the centres of the radicals of the pair at the instant of its formation. Thus in the thermal decomposition (at 65°C) of diacetyl peroxide, where the CH_3 radicals recombining in the cage are separated by two large CO_2 molecules, the yield of ethane (a measure of the cage effect) is 6% and in the photolysis of azomethane, where the methyl radicals are separated only by an N_2 molecule, the yield of ethane is higher by a factor of 10 (65%). Consequently in the absence of inert molecules the radicals in the $[(RO)_3(OH)\dot{P}\ \dot{O}R']$ pair may be side by side and the probability of the cage effect becomes close to unity.

Another kinetic cause of the low number of radicals liberated from the cage may be the high rate of their disproportionation to the reaction products—phosphate and alcohol; the rate constant for this process may be estimated from the experimental data obtained in the present author's study[40] characterising the dependence of the cage effect in the reactions of t-butyl hydroperoxide with triethyl and tripropyl phosphites on the viscosity of the solvent and temperature.

Since it was established[40] that the radicals are released into the bulk phase only by diffusion (the activation energy for the liberation process $E_f \simeq 2.9$ kcal mole^{-1}, a typical value for the activation energy for the diffusion of species in a liquid[66]), in this case the probability of their release is

$$f = \frac{k_{diss}}{k_{diss} + k_{chem}},$$

and its ratio to the probability of disproportionation in the cage is given by

$$\frac{f}{1-f} = \frac{k_{diss}}{k_{chem}}, \qquad (I)$$

where k_{diss} is the rate constant for the dissociation of the pair (s^{-1}) and k_{chem} the rate constant for the chemical monomolecular conversion of the pair into the reaction products (s^{-1}), i.e. the reciprocal of the lifetime of the

pair. Within the framework of the hydrodynamic Stokes–Einstein model, the viscosity and the rate constant for the dissociation of the pair are related by the expression[67]

$$k_{diss} = \frac{6D}{r_0^2} = \frac{kT}{\pi r_0^3 \eta},$$

where η is the viscosity of the medium and D the diffusion coefficient. Since the probability f of the release of radicals from the cage into the bulk phase is smaller by approximately four powers of ten than the probability of the chemical reaction of the pair, Eqn.(I) simplifies to

$$f \simeq \frac{k_{diss}}{k_{chem}},$$

whence after substituting the expression for k_{diss}, it is possible to obtain a relation between f and the viscosity of the solvent at a constant temperature:

$$f = \frac{kT}{\pi r_0^3 k_{chem}} \cdot \eta^{-1} \qquad (II)$$

and between f and T/η at different temperatures in the same solvent:

$$f = \frac{k}{\pi r_0^3 k_{chem}} \cdot T/\eta \qquad (III)$$

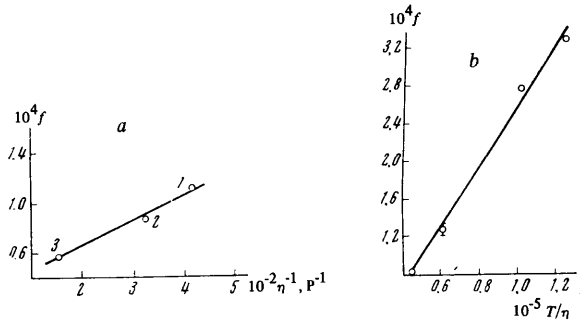


Figure 2. Variation of the number of radicals liberated from the cage into the bulk phase: *a*) with the viscosity of the solvent [according to Eqn. (II)] [1) pentane; 2) hexane; 3) benzene (reaction of t-butyl hydroperoxide with triethyl phosphite at 20°C)]; *b*) with T/η [according to Eqn. (III)] (reaction of t-butyl hydroperoxide with tripropyl phosphite in hexane between −30° and +42°C).

Fig. 2 shows that these formulae hold fairly well under experimental conditions. It follows from both plots that, for an average cage diameter $r_0 = 15$ Å, the rate constant is 1.6×10^{13} s^{-1} (for the reaction with triethyl phosphite) and 4×10^{12} s^{-1} (for the reaction with tripropyl phosphite); these values are close to the frequency of monomolecular decomposition steps; moreover, the linearity of the relation between f and η^{-1} (T = const.) and T/η shows that the rate constant for the disproportionation of radicals within the cage is virtually independent of temperature, as was in fact to be expected.

The kinetic mechanism of the formation of radicals in the reaction of hydroperoxides with aliphatic phosphites can be represented in the following way in a general form:

$$R'OOH + (RO)_3P \xrightarrow{k} \{[R'\dot{O}\overset{-}{O}H \cdots \overset{+}{P}(OR)_3] \rightarrow R'\dot{O}\dot{P}(OH)(OR)_3\} \rightarrow \begin{cases} \xrightarrow{(1-f)k} R'OH + O{=}P(OR)_3 \\ \xrightarrow{fk} R'\dot{O} + \dot{P}(OH)(OR)_3 . \end{cases}$$

In the first stage an electron is transferred from the phosphite to the hydroperoxide with formation of an ion–radical pair; the latter is unstable in neutral solvents and undergoes a monomolecular conversion into a radical pair. The pair disappears mainly by disproportionation within the cage to molecular products—phosphate and alcohol. This mechanism is confirmed by data for radical accepting reactions and chemiluminescence¶; moreover, the idea of electron transfer as the first stage of such reactions is consistent with the capacity of aliphatic phosphites to form paramagnetic charge-transfer complexes (CTC) with typical electron acceptors such as *p*-chloranil[71] trifluoronitrosomethane[72], and others.

Thus the low number of radicals released into the bulk phase (about 10^{-4}) can be explained by such a latent radical mechanism. However, it should be noted that such a low yield may be interpreted also in a different way. It may be assumed that the reaction takes place mainly by non-radical, i.e. ionic or molecular, mechanisms and the contribution of the radical pathway is small (about 10^{-4}). Both alternatives are equivalent in the kinetic sense; therefore, other criteria which would allow a choice will be examined.

One of the characteristics of liquid-phase radical reactions is known to be[73] the cage effect. This effect is associated with the mobility of the species in the liquid phase. Therefore, within the framework of the Stokes–Einstein model, a dependence of the yield of radicals on the viscosity of the solvent is to be expected. Indeed such dependence is found in the reactions of phosphites with hydroperoxides[40,59].

Secondly, the activation energy for the liberation of radicals from the cage into the bulk phase should be close to the activation energy for the diffusion of radicals in the liquid, i.e. 2–4 kcal mole^{-1}.[73] In the reaction of phosphites (tripropyl phosphite in hexane) this energy is 2.9 kcal mole^{-1}.[40]

Thirdly, if the rate constant for the main process is the same in two different solvents with similar viscosities (benzene and styrene) but the yield of radicals in one of them is much higher (more than a factor of ten[59]), one may suppose that the contribution by the radical pathway is much greater. This finding cannot be accounted for without adopting a radical mechanism. It appears that in styrene a new mechanism of the liberation of radicals from the cage, a chemical relay mechanism, obtains; moreover, styrene may affect the lifetime of the radical pair owing to solvation effects.

¶ In principle, the formation of a radical with an unpaired electron at the phosphorus atom as a kinetically independent species is possible also in the reactions of trialkyl phosphites with free radicals, in particular with t-BuO· radicals. Recently this was confirmed experimentally by the observation of the chemically induced polarisation of ^{31}P nuclei in trialkyl phosphates and dialkyl phosphonates[68], by the observation of the ESR spectra of t-butyl radicals[69] as the decomposition products of the primary phosphoranyl radicals $(RO)_3\dot{P}-O-t-\dot{B}u$, and also by the analysis of the distribution of the ^{14}C isotope label in tri-t-butyl phosphate[70].

Furthermore, the finding that the chemiluminescence emitter arises in the cage and not in the bulk phase may serve as evidence that mainly radical processes occur in the cage. However, for a clear understanding of the mechanism of the step in which the emitter is formed, analysis of its excited state is necessary. It was found[64] that, in the reaction of t-butyl hydroperoxide with triethyl phosphite, the phosphate molecule in a triplet state is the chemiluminescence emitter. This finding may be regarded as evidence that the chemiluminescence is a result of the reaction of free radicals only. The following considerations lead to this conclusion. We shall assume that the luminescence arises in the ionic reaction $R'O^- + HO\overset{+}{P}(OR)_3 \rightarrow R'OH + O{=}P(OR)_3$ (according to Denney[55]) as a result of proton transfer from the cation to the anion $R'O^-$. The proton in the cation is weakly bound to the oxygen atom via the lone electron pair of the latter; this means that the P=O bond in the cation already exists and is weakly perturbed by the proton. Therefore the anion, on coming into contact with the cation, "abstracts" the proton, so that the energy of the phosphate molecule produced in this process hardly changes. As a result of this, the entire energy liberated in the recombination of $R'O^-$ and the proton is localised at the alcohol molecule and there is a high probability of its degradation via the internal degrees of freedom. Thus, within the framework of Denney's ionic mechanism, it is difficult to explain the excitation of the phosphate molecule. The localisation of the electron excitation energy at the phosphate molecule is to be expected in the disproportionation of the $R'\dot{O}$ and $HO\dot{P}(OR)_3$ radicals, where the abstraction of a hydrogen atom may lead to the triplet excitation of the double bond in the phosphate.

Finally we may recall that low yields of radicals (about 10^{-3}) are observed also in the benzoyl peroxide–diphenylamine system; this finding was also explained[20] by the high rate of recombination of nitrogen and benzoate radicals in the cage. In this case there is no doubt that the reaction proceeds wholely by a radical mechanism. As will be shown below, in this sense the reactions of amines, phosphites, and also sulphides have common properties and common characteristics.

Thus all the above criteria suggest a latent radical mechanism of the reactions of hydroperoxides with aliphatic phosphites.

Within the framework of the concept of the latent radical mechanism, the mutual enhancement of the effectiveness of phenols and phosphites in the inhibition of the oxidation of polymers can be accounted for[60]; it is due to the high effectiveness of the phosphites in the suppression of degenerate branching.

The kinetics of the reactions of hydroperoxides with aliphatic, aromatic, and mixed phosphites have been investigated in a number of studies by measuring the consumption of the hydroperoxide[59,74,75] and stable radicals[59,60] and by following the chemiluminescence, which was first observed[64] in these reactions. It was found that the rates of the reactions are described by a first-order kinetic equation with respect to each component. Thus the rate constant for the reaction of tri-t-butylphenylphenylene phosphite with 1,1-diphenylethyl hydroperoxide in benzene is described by an equation of the form $k = 2.4 \times 10^8 \exp(-14\,000/RT)$ litre mole^{-1} s^{-1}†; the following expression was obtained for the rate constant for the reaction of tripropyl phosphite with *t*-butyl hydroperoxide in hexane[40]: $k = (0.5 \pm 0.1) \times 10^2 \exp(-5200 \pm 1400/RT)$ litre mole^{-1} s^{-1}. Evidently, as in the case of amines, the reactions of phosphites with hydroperoxides have low activation energies.

† We estimated the values of k_0 and E_{act} from Mukmeneva's data[74].

IV. KINETICS AND MECHANISM OF REACTIONS OF SULPHIDES

We shall now consider the reactions involving sulphides which probably constitute yet another example of oxidation–reduction reactions of peroxy-compounds. In the literature there are several examples confirming this hypothesis. Thus in a study of the effectiveness of the initiation of the polymerisation of methyl methacrylate by various hydroperoxides, Minoura et al.[76] observed an acceleration of the process by the addition of dibenzyl sulphide at 50°C. Kinetic analysis showed that the rate of polymerisation is given by

$$w_n = (k_p/k_t^{1/2})[MMA]^{1.3}[R_2S]^{1/2}[R'OOH]^{1/2}.$$

This shows that the free radicals initiating the polymerisation of methyl methacrylate are formed in a bimolecular reaction of the hydroperoxide and the sulphide; however, it should be noted that Minoura et al.[76] did not estimate the effectiveness of such initiation.

The yield of free radicals in the reactions of hydroperoxides with sulphides (dilauryl thiodipropionate and dibenzyl sulphide) was first measured by Pobedimskii and Buchachenko[77] by the method of stable iminoxy-radicals; it proved to be low (about 10^{-4}). Pobedimskii and Buchachenko[77] suggested a kinetic mechanism for the reaction analogous to that used for the reactions of phosphite[59] (see p. 23). As for phosphites, the low yield of radicals in the reactions of sulphides with hydroperoxides can be accounted for by the closeness of the radicals in the pair and the high rate of their disproportionation to the reaction products; even the addition of radicals to the double bond cannot compete, in terms of rate, with the process taking place within the cage. Thus in styrene, where the rate constant is the same as in benzene, the yield of radicals at 20°C was 3.3×10^{-3}. This example and also the data showing the low yield of radicals in the reactions of amines and phosphites[20,59] illustrate the common latent radical nature of the reactions of sulphides, phosphites, and aromatic amines with peroxy-compounds.

Subsequently Schmidt et al.[78] observed by ESR the formation of the radical-cations of derivatives of diphenyl sulphide [di-(4-methylphenyl), di-(4-methoxyphenyl), di-(4-methoxy-3-methyl), di-(2-chloro-4-methoxyphenyl), di-(4-hydroxyphenyl), di-(3,6-dichloro-4-hydroxyphenyl), and di-(6-chloro-4-hydroxyphenyl) sulphides] in their oxidation by persulphate ions in concentrated sulphuric acid solution at 20°C. For example, the ESR spectrum of the radical-cation of di-(4-methoxyphenyl) sulphide (*g*-factor = 2.0079) consists of nine lines with a splitting of 1.25 Oe owing to the coupling of the unpaired electron with the eight equivalent protons of the aromatic rings (probably the unpaired electron density at the *ortho*- and *meta*-protons is the same); the observed ratios of the hyperfine structure intensities (0.6 : 7 : 27 : 54 : 70 : 53 : 23 : 4 : 0.6) proved to be close to the ratios expected for the proton structure (1 : 8 : 28 : 56 : 70 : 56 : 28 : 8 : 1). The isolation of the radical-cations in a pure state in 100%

yield (as the hexachlorostannate) unambiguously demonstrates that the reaction investigated takes place exclusively via one-electron transfer.

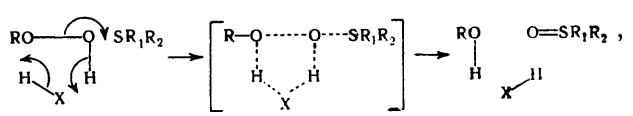
The radical cations $CH_3O-C_6H_4-\overset{+\cdot}{S}-C_6H_4-OCH_3$

were detected[77] also in the reactions of cumenyl peroxide, benzoyl peroxide, and dicyclohexyl peroxydicarbonate with the initial sulphide in trifluoroacetic acid and in its mixtures with polar solvents (i.e. in media where the radical cations are stabilised). The experimental hyperfine coupling constants ($a_H^o = a_H^m = 1.35$ Oe) are close to those measured for the same radical-cations obtained in the oxidation by persulphate ions[78]. This result is important; it can be regarded as confirmation of the suggested mechanism for the formation of free radicals in the reaction of hydroperoxides with aliphatic sulphides[77].

In a number of studies the products and the kinetics of the reactions of peroxy-compounds (diacyl peroxides, peracids, and hydroperoxides) with sulphides were investigated. At moderate temperatures benzoyl peroxide and hydroperoxides usually yield only the sulphoxides $R_2S{=}O$, whereas peracids convert sulphides via sulphoxides into sulphones R_2SO_2.[27,28,79] The rates of these two stages differ significantly; for example, peracetic acid in acetic acid solution oxidises diphenyl sulphide to the sulphoxide about 1000 times faster than the oxidation of the sulphoxide to the sulphone[80]. Horner[81,82] showed that the reactions of sulphides with benzoyl peroxide in chloroform are described by a second-order kinetic equation; aliphatic sulphides reacted at 20°C faster than aromatic sulphides [the rate constant for the reaction of $(C_2H_5)_2S$ is about 3.6×10^{-3} litre mole^{-1} s^{-1} and that for the reaction of $C_2H_5SC_6H_5$ is 4.5×10^{-4} litre mole^{-1} s^{-1}]. Overberger and Cummins[83] found that the reduction of peracids by sulphides also follows second-order kinetics.

The kinetics of the reaction of hydroperoxides with sulphides were investigated in protic and aprotic solvents simultaneously by iodometric titration of the hydroperoxide and chemical determination of the reaction product (the sulphoxide)[27,28,79,84,85]. In alcoholic, aqueous alcoholic, acidic, and basic solutions at temperatures between −65° and +75°C the reaction has the following parameters: (1) 1 : 1 stoichiometry according to the equation $R_2S + R'OOH \rightarrow R_2SO + R'OH$; (2) first order with respect to each component; (3) low activation energies (between 9.5 and 17.5 kcal mole^{-1} depending on the structure of the hydroperoxide[79]; (4) specific Brönsted acid catalysis at pH < 3.[85]

In aprotic solvents unusual kinetic relations were observed. Thus Bateman and Hargrave[84] found that the rate of the reaction of cyclohexyl methyl sulphide with t-butyl hydroperoxide in benzene at 50°C obeys a second-order kinetic equation with respect to the hydroperoxide, while in a benzene–acetic acid (or alcohol) mixture the hydroperoxide is consumed according to first-order kinetics. It was suggested[79,84] that this reaction has a molecular mechanism without the formation of free radicals, via the transfer of a hydrogen atom in a cyclic activated complex:



where X = CH_3COO, ROO, or RO.

However, many facts cannot be explained by the proposed mechanism[79,84] [different kinetic effects of the hydrogen bonds between the hydroperoxide and the molecules of the medium (methanol or acetic acid), unequal effects of the inhibitors and oxygen on the rate of reaction as a function of the solvent, fractional order of the reaction with respect to the sulphide in the absence of oxygen, etc.] and therefore the findings in these investigations cannot be regarded as unambiguous. Moreover, the destruction of stable radicals following their introduction into the hydroperoxide–sulphide system (in the presence of the sulphide alone or the hydroperoxide alone, stable radicals are not consumed)[77] and also the initiation of the radical polymerisation of methyl methacrylate by a hydroperoxide–sulphide system[76] are completely inconsistent with the hypothesis of a molecular mechanism; moreover, the type of relation between w_n and the concentrations of the sulphide and the hydroperoxide corresponds to bimolecular formation of radicals (and not trimolecular as would be expected according to Bateman and Hargrave[84]). A polarographic study of the consumption of t-butyl hydroperoxide in the reaction with dilauryl thiodipropionate at 20°C in benzene also led the authors[77] to the conclusion that the reaction in benzene is of first order with respect to each component.

Thus the detection of radical-cations and free radicals in various sulphide–peroxy-compound systems permits the hypothesis of the existence of a single mechanism for all the reactions of sulphides: it suggests that the reactions following electron transfer have a radical mechanism. Within the framework of these concepts, it is possible to explain also the significance of the specific acid catalysis of the reactions of sulphides with hydroperoxides[85]; it is probably due to the fact that electron transfer from the sulphide molecule to the hydroperoxide takes place with participation of the protonated form of the latter, which is more reactive (a more powerful electron acceptor) than the free hydroperoxide.

V. OXIDATION–REDUCTION NATURE OF THE REACTIONS OF PEROXY-COMPOUNDS WITH PHOSPHITES, SULPHIDES, AND AROMATIC AMINES

An interesting and general result of the reactions of peroxy-compounds with amines, phosphines (and hence also phosphites), and sulphides is, as shown below, the existence of correlations of the Hammett equation type for the rates of these reactions and also correlations between the rate constants and ionisation potentials and electron affinities; the occurrence of identical correlations implies that the mechanisms of all three types of reaction are governed by a common relation. We shall examine these correlations and shall attempt to account for them in terms of an oxidation–reduction mechanism.

From the standpoint of Mulliken's theory[86], electron transfer in a donor–acceptor pair takes place between the higher filled molecular orbital (MO) of the donor and the lower vacant molecular orbital of the acceptor. Calculation of the electronic structures of the various peroxy-compounds by the extended Hückel method[87-89] showed that the lower vacant molecular orbital of these compounds is an antibonding orbital localised in the $2p\sigma$-orbital between two oxygen atoms.

One may suppose that the introduction of electron-accepting substituents into the peroxide and of electron-donating substituents into the donor molecule will lead respectively to a decrease of the energy level of the

antibonding orbital along the O–O bond in the peroxide and to an increase of the level of the donor orbital filled by the lone electron pair.

Bearing in mind that the rates of the reactions of peroxy-compounds with amines, phosphites (phosphines), and sulphides are probably determined by electron transfer from the donor to the peroxide, such mutual approach of the energy levels of the reactants on introduction of polar groups will result in a lowering of the activation energy for the process and hence in an increase of its rate constant.

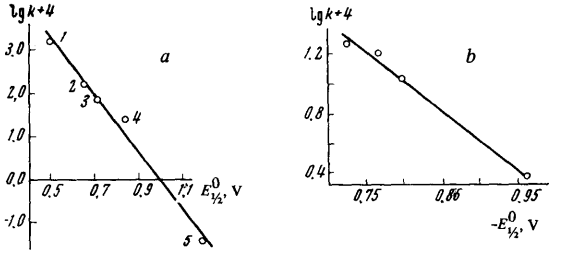


Figure 3. Variation of the logarithm of the rate constant: *a*) with the half-wave oxidation potential for the reaction of benzoyl peroxide with dimethylaniline and its *para*-derivatives [1) CH_3O; 2) CH_3; 3) H; 4) Cl; 5) NO_2]; *b*) with the half-wave reduction potential for the reaction of cyclohexyl methyl sulphide with various hydroperoxides.

Indeed the literature data show that many of the reactions considered here obey the Hammett relation. For example, electron-donating substituents in the benzoyl peroxide molecule decrease the rate of its reaction with dimethylaniline ($\rho = +0.181$).[14] The effect of the substituents in the ring of the dimethylaniline molecule on its reaction with benzoyl peroxide is of the opposite type ($\rho = -4.25$; this value was determined by the present authors from the data of Horner and Scherf[81] for σ° in the range between −0.27 and +1.27‡); then the rates of the reactions of amines with the most electron-accepting and electron-donating substituents differ by a factor not less than 10^3§. Ring substituents have an analogous effect on the rate of reaction of methyl phenyl sulphide with benzoyl peroxide: in the extreme cases the rates of reaction differ by a factor of about 200.[82] However, the slope of the correlation line was smaller ($\rho = -2.2$; this value was determined by the present authors from the data of Horner and Jügens[82] with σ° in the range between −0.27 and +0.78); probably, the effect of substituents on the position of the donor level in the sulphide is somewhat reduced compared with the analogous effect in the amine. Finally, it is known[49] that the reaction of phosphines and benzoyl peroxide is also accelerated by the introduction into the peroxide molecule of electron-accepting substituents.

The rates of the reactions of benzoyl peroxide with dimethylaniline and its *para*-substituted derivatives show an explicit relation also with the polarographic oxidation potentials of the donor molecules. This relation can be understood if one takes into account the fact that the energies of the highest filled orbitals are frequently correlated with the first polarographic oxidation half-wave potential; in this case such a potential corresponds to the first oxidation stage—the abstraction of one electron from the amine molecule with formation of a radical–cation. Table 3 lists the literature values of the rate constants for the reaction of benzoyl peroxide with dimethylaniline and its *para*-substituted derivatives, the first polarographic half-wave oxidation potentials $E^0_{1/2}$ for which are known.

Table 3. Data for the rates of reaction of benzoyl peroxide with dimethylanilines*.

para-Substituent	$E^0_{1/2}$ (in acetonitrile)	$10^4 k_{20°}$, litre mole^{-1} s^{-1}	Solvent in reaction
CH_3O	0.48	1550	Chloroform
CH_3	0.65	166	ditto
H	0.71	76	»
Cl	0.84	26	»
NO_2	1.19	0.04	»

* The values of k were taken from Horner and Scherf[81] and those of $E^0_{1/2}$ from Seo et al.[92]

Fig. 3 shows the variation of the logarithm of the rate constant with the oxidation half-wave potentials of amines which the present authors plotted from the data in Table 3. Evidently the experimental data fit on a straight line described by the empirical equation $\lg k_1 - \lg k_2 = \alpha(E^0_{1/2(1)} - E^0_{1/2(2)})$, where $\alpha = -6.6$. This relation arises in consequence of the general relation between the affinity of the reaction (the free energy change) and its rate, since the affinity of the reaction in the cases under consideration is determined primarily by the difference between the energies of the lowest vacant molecular orbital of the peroxy-compound and the highest filled molecular orbital of the donor.

Another relation is also to be expected: the relation between the rate constants and the second component of the reaction affinity (the energy of the lowest vacant molecular orbital of the acceptor). The polarographic reduction half-wave potential $E^0_{1/2}$ may serve as a measure for the comparison of the electron-accepting properties. It is known[93] that hydroperoxides are reduced at a dropping mercury electrode by a two-electron process:

$$R'OOH \xrightarrow[+2e^-]{+2H^+} R'OH + H_2O$$

and give rise to a single polarographic wave. If it is assumed that the rate-limiting stage in the electrochemical reduction of the hydroperoxide is the transfer of the first electron, then the experimental value of $E^0_{1/2}$ must correspond to the one-electron reduction of the hydroperoxide $R'OOH + e \rightarrow R'\dot{O}\bar{O}H$ and consequently can serve

‡ The values of σ° recommended by Taft[90] and Jaffe[91] were employed.

§ Attention should be drawn to the fact that the rate constant for the reaction of benzoyl peroxide with dimethylaniline and its derivatives and the hyperfine coupling constants for the ^{14}N nucleii in the radical-cations (see Fig. 1) vary in the opposite sense on introduction of electron-accepting groups into the aromatic ring; this implies that the a_N/σ correlation has a direct bearing on the reactivity of dimethylaniline and its derivatives.

as a measure of its electron affinity. Using this approximation, we shall attempt to find a relation between the rate constants and the potentials $E^0_{1/2}$.

Comparison of the rate constants for the reactions of various hydroperoxides with cyclohexyl methyl sulphide (Table 4) and the data for their polarographic reduction shows that the rate constant increases as the negative value of $E^0_{1/2}$ diminishes.

Table 4. Data for the rates of reaction of cyclohexyl methyl sulphide with various hydroperoxides (at 50°C in methanol)*.

Hydroperoxide	$E^0_{1/2}$ (in methanol–benzene)	$10^4 k_2$, litre mole^{-1} s^{-1}	E_{act}, kcal mole^{-1}	$10^{-5} k_0$, litre mole^{-1} s^{-1}
$(CH_3)_3COOH$	−0.96	2.2	14.1	7.6
–OOH	−0.80	10.8	—	—
–OOH	−0.77	16.5	12.6	3.1
–OOH	−0.73	18.4	—	—

* The values of k were taken from Bentrude and Wielesek[70] and those of $E^0_{1/2}$ from Willits et al.[94]

Fig. 3*b* shows this relation in a semilogarithmic form, which, like the relation for the amines (Fig. 3*a*), is satisfactorily consistent with the familiar Dimroth equation[95] for oxidation–reduction reactions: $\lg k_2 - \lg k_1 = \beta(E_2 - E_1)$; for the sulphide, the difference between the redox potentials $E_2 - E_1$ is equivalent to the difference between the reduction half-wave potential $E^0_{1/2(2)} - E^0_{1/2(1)}$ and the slope $\beta = +4.2$.

The existence of Hammett type correlations for the rates of the reactions of peroxy-compounds with amines, phosphines (and, by analogy, with phosphites), and sulphides and also the correlations between the rate constants and the ionisation potentials and electron affinities may serve as an indication that in the activated complex an electron is transferred and that this stage is probably rate-limiting.

In conclusion we may note that many reactions are considered to be ionic or molecular only because free radicals are not detected during their occurrence; in fact, however these reactions can frequently be of the latent radical type, i.e. they can proceed via free radicals which are destroyed in the cage immediately after their formation. Clearly new approaches and new ideas are required in order to be able to control processes within the cage by actively interfering with their kinetics. One of such approaches may be the study of dynamic nuclear polarisation in chemical reactions[96].

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