Decomposition of Peroxybenzoic Acid in Solution. VI. Theoretical Consideration of the Induced Decomposition of Peroxides by Radicals

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In the previous parts of this series$^{1-5)}$ it has been shown that one of the notable features of the decomposition of peroxybenzoic acid in various solvents is its very facile decomposition, induced by radicals (R·) generated in solution; this takes place according to the following equation:

$$\mathrm{PhCO_3H + R\cdot \rightarrow PhCO_2\cdot + ROH} \qquad (1)$$

A similar induced decomposition by radicals is generally recognized to occur with various peroxides (POOP')$^{6,7)}$ with varying degrees of readiness according to the following equation:

$$\mathrm{POOP' + R\cdot \rightarrow ROP + P'O\cdot} \qquad (2)$$

Thermochemical consideration shows that the induced decomposition takes place exothermically. Thus, since the heat of reaction $(-\varDelta H)$ is gvien by the difference in bond dissociation energy (D) between the bond formed and the one broken,

$$(-\varDelta H) = D(\mathrm{R{-}OP}) - D(\mathrm{PO{-}OP'})$$

the heat of reaction for the induced decomposition will be 50∼60 kcal./mol., if we assume the generally accepted values of 90$^{8)}$ and 30∼40 kcal./mol.$^{6)}$ for D(R–OP) and D(PO–OP') respectively. In fact, in accordance with such large exothermicity, the activation energy for the induced decomposition of peroxybenzoic acid by the polymethyl methacrylate radical has been shown to be 6.6 kcal./mol.$^{9)}$, indicating that this reaction takes place very easily. If the activation energy changes parallel with the heat of reaction, as is usually the case with many reactions, e. g., the abstraction of a hydrogen atom from hydrocarbon by a variety of alkyl radicals$^{10)}$, the resonance stabilization on the part of the attacking radical would reduce the heat of reaction and would, therefore, be expected to enhance the activation energy thus making the radical the less reactive.

However, the reactivity of a radical in the induced decomposition of peroxides appears to be affected not so much by the resonance stabilization of the radical as by its electron-donating property. Thus, our results$^{1-5)}$ show that radicals derived from alcohols and ethers, $\mathrm{RR'\dot{C}OR''}$, appear to be the most active; then come the hydrocarbon radicals, e. g., the cyclohexyl radical, and the trichloromethyl radical seems to be least reactive, being unable to cause the induced decomposition of peroxybenzoic acid. This trend suggests that the more electron-donating radical is the more reactive. A similar trend has been observed

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9) H. Terada, *Yuki Gosei Kagaku Kyokaishi*, **20**, 158 (1962).
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in the induced decomposition of benzoyl peroxide[6,7,11,12]. Mashio and Kato[13] have shown that the reactivity of radicals derived from various alcohols towards benzoyl peroxide decreases in the order: 1-hydroxy-1-methylethyl > 1-hydroxyethyl > hydroxymethyl. Apparently this is the order of decreasing electron-donating property as well as the order of decreasing resonance stabilization. Thus we are led to the conclusion that the more electron-donating radical is more reactive in the induced decomposition of peroxides, even if it is the more resonance-stabilized radical.

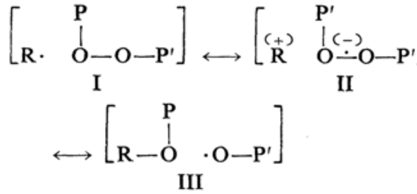
The way in which change in the structure of a radical affects its electron-donating property and the extent of resonance stabilization, leading to the above sequence in regard to those two respects, is understood in terms of a molecular orbital theory. A treatment of 1-hydroxyalkyl radicals according to a simple LCAO-MO method with regard to an odd electron on the carbon and two lone-pair electrons on the oxygen atom shows that the radical as a whole is stabilized with respect to the state in which the odd electron and the lone-pair electrons are localized on the carbon and the oxygen atom respectively; that the molecular orbital occupied by the odd electron is located at a higher energy level than the orbital when the odd electron is localized; and that the more stabilized the radical becomes, the higher the level of the odd electron tends to lie. Obviously such results will generally be obtained when a group carrying a lone-pair of electrons or a group capable of hyperconjugation like a methyl is placed in juxtaposition with the radical centre.

The energy level of the highest occupied orbital is related to the ionization potential of this chemical species in such a way that the higher the former is, the smaller is the latter. For lack of appropriate experimental data for hydroxyalkyl radicals for comparison with the theoretical deduction, we quote the values for alkyl radicals in Table I to show the effect on the resonance energy and the ionization potential brought about by the introduction of an increasing number of electron-releasing methyl groups into a methyl radical. The trend which is apparent in the table is in keeping with the foregoing theoretical prediction.

TABLE I. RESONANCE ENERGIES AND IONIZATION POTENTIALS OF ALKYL RADICALS

Radical	Resonance energy[14] in kcal./mol. Calcd.	Obs.	Ionization Potential[15] in eV.
Methyl	—	—	9.85
Ethyl	7.05	7.2	8.66
n-Propyl	8.6	8.1	7.57
Isopropyl	14.1	12.6	7.45
t-Butyl	21.2	16.7	6.90

The view that the electron-donating property is a factor of primary importance in determining the reactivity of radicals in the induced decomposition under consideration suggests that interaction of the charge-transfer type[16] between an attacking radical as a donor and a molecule of a peroxide as an acceptor is important. This charge-transfer interaction is thought to take place, to the first approximation, between the highest occupied orbital on the radical and the vacant antibonding orbital, $2p\sigma_u$, around the oxygen to oxygen bond in the peroxide. Evidently such a low-lying vacant orbital is responsible for the oxidative action in general or for the electron accepting property of peroxides. Thus, the transition state of the induced decomposition may be schematically expressed by the following structures, form II representing the interaction of the charge-transfer type, which contributes to lowering of the energy of the transition state:



$$\underset{\mathrm{I}}{\left[\mathrm{R}\cdot\quad \overset{\mathrm{P}}{\overset{|}{\mathrm{O}}}-\mathrm{O}-\mathrm{P'}\right]} \longleftrightarrow \underset{\mathrm{II}}{\left[\overset{(+)}{\mathrm{R}}\quad \overset{\mathrm{P'}}{\overset{|}{\mathrm{O}}}\overset{(-)}{\dot{-}}\mathrm{O}-\mathrm{P'}\right]}$$

$$\longleftrightarrow \underset{\mathrm{III}}{\left[\mathrm{R}-\overset{\mathrm{P}}{\overset{|}{\mathrm{O}}}\quad \cdot\mathrm{O}-\mathrm{P'}\right]}$$

Since such a polar-resonating structure contributes to the structure of the reacting system in charge-transfer interaction, polar solvents like alcohols and ethers would further lower the energy of the system by solvation.

According to the accepted theory[16], the lowering in energy of the reacting system due to the charge-transfer interaction is approximately inversely proportional, other things being equal, to the difference in energy between the highest occupied orbital of the radical and the $2p\sigma_u$ orbital of the peroxide, or to the difference between the ionization potential of the radical and the electron affinity of the $2p\sigma_u$ orbital. Thus, the higher the energy level of the orbital occupied by the odd electron in a radical, the larger is the extent of the charge-transfer, with a corresponding lowering in energy, and, therefore, the more reactive

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the radical becomes. This prediction is in agreement with the observed trend in the reactivity of radicals in the induced decomposition.

In the charge-transfer type of interaction, not only the energy difference between the participating orbitals, but also their overlapping, is important. Therefore, the introduction of a bulky group around the radical centre will hinder the overlap sterically, and the introduction of a conjugating group will do so by reducing the electron density at the radical centre of the orbital occupied by the odd electron. In fact, Mashio and Kato[13] have shown that the reactivity towards benzoyl peroxide of radicals derived from primary alcohols decreases as the alkyl chain lengthens. Further, they have shown that the reactivity of the radical derived from benzyl alcohol is twice as large as that from α-tetralol. This difference is probably due to steric hindrance of the overlapping of the relevant orbitals in the charge-transfer interaction, since the energy level of the highest occupied molecular orbital is almost the same for these two radicals. The fact that the reactivity of the radical derived from benzhydrol is lower than that from benzyl alcohol is probably due to the same steric effect as well as to the more extensive delocalization of the odd electron in the former radical.

The rate constant for the chain transfer to a substituted benzoyl peroxide by polymer radicals is known to increase according as the substituent group becomes more electron-attracting[17,18]. This fact is readily understood in light of the fact that an electron-attracting group lowers the energy level of the $2p\sigma_u$ orbital around the oxygen to oxygen bond, resulting in a stronger charge-transfer interaction between the attacking radical and the peroxide, with a corresponding reduction of the activation energy.

The chain transfer constant by the polymer radical generally appears to be larger for hydroperoxides than for benzoyl peroxide[18,19], and as has been previously pointed out[5], peroxybenzoic acid is attacked by radicals more readily than benzoyl peroxide, although benzoyl peroxide might be expected to be more reactive, since the benzoyl group is more electron-attracting than the alkyl group or the hydrogen atom. The disagreement probably is attributable to steric hindrance by the bulky benzoyl group of the overlapping of the two interacting orbitals participating in the charge transfer.

In the induced decomposition of benzoyl peroxide, Swain, Stockmayer, and Clarke[17] have pointed out a contribution of polar resonance structures in which the odd electron is found transferred on the molecule of the peroxide because of the presence of the electron-withdrawing carbonyl group. It is apparent from the foregoing discussion, however, that it is the vacant orbital around the oxygen to oxygen bond that is important in a charge-transfer type interaction in the induced decomposition, and that the role of the carbonyl group, if present in the molecule, is subordinate.

Obviously the charge-transfer concept may readily be applied to the elucidation of the reactions of peroxides with anionoid reagents in general, the nucleophilic attack by the latter being ascribed to the presence in the former of a vacant orbital which is able to accept an electron readily. To cite a few examples, in the reaction of benzoyl peroxides with *N*,*N*-dimethylanilines, an electron-attracting substituent in the former[20] and an electron-repelling substituent in the latter[21] both accelerate the reaction. This fact can be explained as due to the lowering of the energy level of the antibonding orbital of the oxygen to oxygen bond and to the elevation of that of the lone-pair orbital on the nitrogen atom, the charge-transfer interaction being thus made much easier. It is to be noted in this connection that Imoto and Choe[20] have suggested the coordination of the lone-pair electrons on the nitrogen atom with the peroxidic oxygen. Similarly, reactions of substituted benzoyl peroxides with alkali iodides[22] or with phosphines[23], and reactions of peroxybenzoic acid with olefins[24], sulphides[25] and sulphoxides[26] and the oxidation of sulphides with hydrogen peroxide[27] are to be understood in terms of the charge-transfer interaction.

In the reaction of peroxides with cationoid reagents, e. g., ions of transition metals in the higher oxidation state and Lewis acids, another type of charge-transfer interaction is possible, an interaction in which a lone-pair orbital at

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a peroxidic oxygen atom will act as an orbital of the donor type.

The polar effect in radical reactions may generally be interpreted as arising from the change in the magnitude of the charge-transfer interaction between radicals and substrates due to the change in energy level of the interacting orbitals.

Summary

On the basis of observations on the induced decomposition of peroxides by radicals, it has been suggested that the interaction of the charge-transfer type, involving the highest occupied molecular orbital in an attacking radical and the $2p\sigma_u$ antibonding orbital around the oxygen to oxygen bond in a molecule of peroxide, contributes to a lowering of the activation energy of reaction. Possible extension of this idea to elucidation of the reactions of peroxides with other reagents has been pointed out.

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