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Does Reduction of Organic Peroxides by Iodide Ions Really Proceed via Single Electron Transfer?

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The mechanism for reactions of diaroyl peroxides with I^- commonly utilized for their determination is reexamined in terms of single electron transfer (SET) theory and is regarded not as an SET mechanism as has been supposed but an S_N2 mechanism.

Recently, many organic reactions have been shown to proceed through single electron transfer (SET) [1] and its participation is argued in terms of electron transfer theory [2,3] or the potential energy surface of the reactions.[4] As a result, the relationship between S_N2 and SET becomes one of the fundamental problems in contemporary physical organic chemistry.[4a] This recent trend has prompted us to reexamine on the ground of SET theory whether reduction of organic peroxides by iodide salts widely used for their determination does proceed by the way of either SET or S_N2 mechanism. The bimolecular reaction between KI and various substituted benzoyl peroxides was previously shown by Tsuchihashi et al. to obey Hammett's relationship with a reaction constant, ρ, +0.756 in ethanol [5] and generally supposed to take place through SET.

$$2I^- + (PhCO_2)_2 \rightarrow I_2 + 2PhCO_2^-$$

SET Mechanism

$$\begin{aligned} I^- + (PhCO_2)_2 &\rightarrow I\cdot + PhCO_2\cdot + PhCO_2^- \\ I^- + PhCO_2\cdot &\rightarrow I\cdot + PhCO_2^- \\ 2I\cdot &\rightarrow I_2 \end{aligned}$$

S_N2 Mechanism

$$\begin{aligned} I^- + (PhCO_2)_2 &\rightarrow PhCO_2I + PhCO_2^- \\ PhCO_2I &\rightarrow PhCO_2\cdot + I\cdot \\ I^- + PhCO_2I &\rightarrow I_2 + PhCO_2^- \\ I^- + PhCO_2\cdot &\rightarrow I\cdot + PhCO_2^- \\ 2I\cdot &\rightarrow I_2 \end{aligned}$$

If the above reaction proceeds via SET, according to Marcus's theory,[2] the free energy of activation ($\Delta G^{\neq}$) is to be correlated with the free energy change (ΔG^o) for SET through a reorganization energy (λ) as expressed in the following equation which affords parabolas between $\Delta G^{\neq}$ and ΔG^o depending on λ values. λ corresponds to $4\ \Delta G^{\neq}(0)$; $\Delta G^{\neq}(0)$ means the free energy of the activation when $\Delta G^o=0$.

$$\Delta G^{\neq} = (\lambda/4)\ (1 + \Delta G^o/\lambda)^2$$

Accordingly, the rate constant for SET, k_{obs}, is to be shown by the following equation where A is usually between 1-0.2.

$$k_{obs} = kd/\left[1+A \exp\{(\lambda/4)(1+\Delta G^o/\lambda)^2\}\right]$$

This treatment can be revised in several ways. One of those is the following Agmon-Levine's formula which is supposed to be appropriate when $\Delta G^{\neq}(0) \ll |\Delta G^{o}|$.[3)]

$$\Delta G^{\neq} = \Delta G^{o} + \frac{\Delta G^{\neq}(0)}{\ln 2} \ln\left\{1 + \exp\left[\frac{\Delta G^{o}\ln 2}{\Delta G^{\neq}(0)}\right]\right\}$$

The kinetic data for reactions between KI and a series of substituted benzoyl peroxides in ethanol determined by Tsuchihashi et al.[5)] are now reexamined in terms of electron transfer theory. To estimate ΔG^{o} value for this reaction, $\Delta G^{o} = E^{o}(BPO/PhCO_2\cdot{+}PhCO_2^-) - E^{o}(I\cdot/I^-)$, the former is put as 0.1 V vs. NHE; [1a, 6)] $E^{o}(I\cdot/I^-)$ corresponding to single electron redox system between I· and I^- is taken as 1.2 V (in CH_3CN) vs NHE which was estimated from the conventional standard electrochemical potential for two electron redox system between I_2 and $2I^-$ with thermochemical corrections for formation of iodine molecule.[1a)] Among the substituted BPO's, the electrochemical potential for 4,4'-dinitro and dichloro BPO are estimated as 0.08 and 0.02 V more anodic than for BPO; those for 4,4'-dimethyl and dimethoxy BPO are 0.015 and 0.02 V more cathodic.[7)]

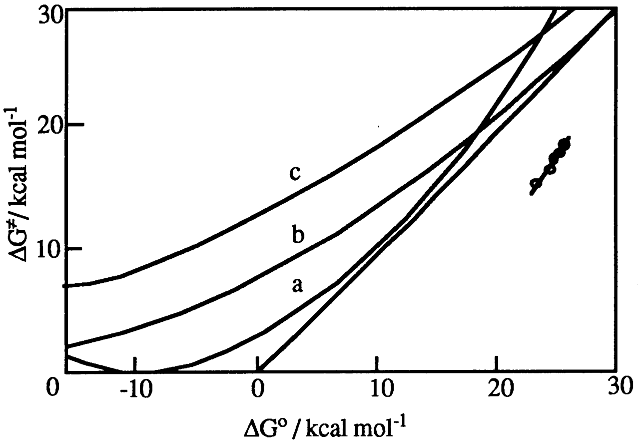


Fig.1. Plots of $\Delta G^{\neq}$ against ΔG^{o} according to Marcus's treatment. Curves a, b and c correspond to λ = 10, 30, and 50 kcal mol^{-1}, respectively,[1b)] and the straight line is for $\Delta G^{\neq}=\Delta G^{o}$.

We attempted to plot the reported data both in Fig. 1 according to Marcus's equation [1)] and in Fig. 2 prepared following Agmon-Levine's equation.[3b)] However, the both plots are much more deviated from the ordinary region of the relationship. As an example, for I^- - BPO proceeding with a rate constant of nearly 4×10^{-1} dm^3 mol^{-1} s^{-1} at 300 K, $\Delta G^{\neq}$, 18.1 kcal mol^{-1} (1 kcal = 4.184 kJ),[5)] is considerably lower than ΔG^{o} estimated as 25.3 kcal mol^{-1} which could not give a reasonable λ value.

The value of ΔG^{o} may be accompanied by uncertainty in the estimation of $E^{o}(BPO/PhCO_2\cdot{+}PhCO_2^-)$ in irreversible reduction of the peroxide. Eberson suggested to shift the E^{o} value for BPO even 0.5 V more anodic considering a large overpotential to be supposed for its electrode process, and further suggested that SET to peroxides will proceed with a large reorganization energy such as 40 kcal mol^{-1} [1c)] due to the cleavage of the peroxide linkage to benzoyloxyl radical and benzoate anion. Accordingly, we attempted to shift E^{o} value for BPO as above, however, it still gives a plot in the region of smaller reorganization energies than suggested by Eberson.[1c)]

Therefore, it is probable that the reaction does not proceed through SET mechanism but takes place through S_N2 mechanism giving benzoylhypoiodide $PhCO_2I$. Production of chlorobenzene in the reaction between Cl^- and BPO in acetonitrile at 98 °C probably by the way of $PhCO_2Cl$ [8)] can support the formation of $PhCO_2I$ as an intermediate in the reaction of BPO with I^-.

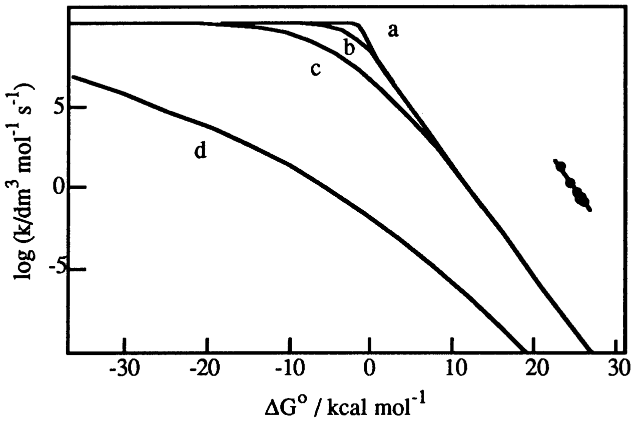
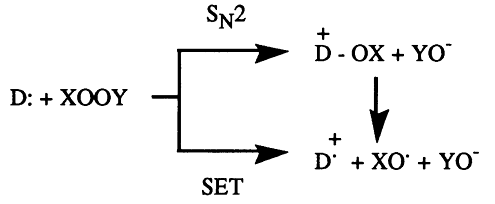


Fig. 2. Plots of log ($k/dm^3\ mol^{-1}\ s^{-1}$) at 25 ℃ against ΔG° according to Agmon-Levine's formula.[3b)] Curves a, b, c, and d correspond to $\Delta G^{\neq}(0)$=1, 5, 10, and 20 kcal mol^{-1}, respectively.

Reexamination can be extended to various reactions of organic electron donors or anionoid reagents like amines with diaroyl peroxides investigated since 1950's;[9)] previously we argued these reactions in terms of charge transfer from the donors to the antibonding σ orbital of the peroxide linkage.[10)]

Generally, reactions of anionoid reagents (D:) with organic peroxides (XOOY) could be described through either S_N2 accompanied by charge transfer or SET as written below.[10-12)]



D: ; I^-, R_3N:, R_2S:, R_3P:

X,Y: ArC(=0)

Among the reactions between various organic electron donors and diaroyl peroxides [13)], the reaction between N,N-dimethylaniline (DMA) and BPO [9)] was argued by Eberson to show that the reported rate constant, 1.1 x 10^{-3} $dm^3\ mol^{-1}\ s^{-1}$ (35 °C), could feasibly agree with the value estimated according to Marcus's theory assuming a very large λ value, 40 kcal mol^{-1}.[1a, 1c)] However, attempted plot in Fig. 1 of its observed $\Delta G^{\neq}$ value (13.0 kcal mol^{-1} at 300 K) against ΔG° value for SET, 21.4 kcal mol^{-1} (estimated from $E^{o}(DMA^{+\cdot}/DMA)$ = 1.03 V [15)] and E^{o}(for BPO) = 0.1 V vs. NHE), shows that this reaction could not take place via SET.[14)] Furthermore, isolation of ammonium salt from the reaction between triethylamine and diacetyl peroxide,[16)] formation of products derived from intermediate ammonium salts in the reaction of DMA with aroyl cyclobutanoyl and cyclopropylaceyl peroxide,[6)] the observed reverse hydrogen isotope effect in the reaction of deuterated sulfide and BPO [11)] as well as the observed not highly selective orientation of DMA on 4-methoxy-4'-nitro BPO [17)] can be taken to support S_N2 rather than SET.

The present consideration in terms of SET theory indicates that the reactions between anionoid reagents and organic peroxides, if considerably endergonic, do not tend to proceed through SET except special cases [6)] but proceed through S_N2. The anionoid orbital will take preferable orientation to the peroxide linkage as evidenced by negative activation entropy (-20.4 and -9.9 cal $K^{-1}\ mol^{-1}$ for I^- [5)] and DMA [9)] with BPO respectively) accompanied by transfer of negative charge leading to the cleavage of the peroxide.[18)]

While I was working graduate research from 1950's to early 1960's with Professor Emeritus Osamu Simamura, The University of Tokyo, I was very much interested in the charge transfer nature of the various

reactions of organic peroxides through stimulated works there and by Professor Emeritus Minoru Imoto, Osaka City University and Professor Tadashi Suehiro, Gakushuin University. The author thanks those professors. The author is also grateful to Professor Waldemar Adam in the University of Wurzberg, Germany for his discussion prompting me to reinvestigate this task and sending me his unpublished results, and to Drs. Ken Fujimori and Tatsuo Arai in this university for their stimulating discussion.

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