A Simple Model for Diffusive Behavior of Reactive Radical Pairs

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Abstract: A simple model is derived to account for the diffusive behavior of radical pairs which are destroyed rapidly. The implications of this model are discussed.

The operation of geminate oxy–oxy radical recombinations has been demonstrated recently through several independent lines of investigation. The oxygen-18 equilibration of carbonyl-labeled acetyl peroxide[1] and *t*-butyl peracetate,[2] which occur at rates comparable to those for the over-all destruction of the peroxides, have been interpreted in terms of reversible radical pair formation. The isolation of di-*t*-butyl peroxide,[3] *t*-butyl perbenzoate,[4] and *t*-butyl peracetate[2] from the low-temperature decomposition of the corresponding dialkyl and acylalkyl hyponitrites suggests that this type of behavior is probably general. The rates of over-all destruction of a large number of initiators decrease with increasing viscosity of the medium.[5] These changes have also been interpreted in terms of reversible radical pair formation.

While the qualitative concept of geminate combination of radical pairs is common in the interpretations provided for all of these recent observations, the quantitative aspects of the results are less settled. Both the yield and rate (Figure 1)[6] functions have been observed to be more nearly correlated with the square root than the first power of fluidity[7] (reciprocal viscosity, $1/\eta$). We have recently[2] proposed an approximate justification for this square-root dependence by assuming that the *effective* rate constant (k_d) for reaching a diffusively separated state was related to the root-mean-square displacement distance[8] of the radical pair during its average lifetime. The present paper gives a somewhat more rigorous derivation of this relationship and provides a discussion of the implications of the model.

Results and Discussion

In general, a radical pair can be considered to be created, by a chemical reaction in solution, within a cylindrical volume element of arbitrary height, ρ. One of the reaction paths available to this pair is diffusive displacement outside of this original volume element. If we assume that the coordinate system which refers to this volume element is undergoing rotation and translation with the symmetry axis of the radical pair, then the problem of diffusive displacement reduces to that of diffusion from a finite cylinder in one dimension. The one dimensional character of this model is not as bad as it might seem since this one dimension can be thought of as the reaction coordinate for the diffusive reaction path which is open to the pair. For reactive radicals, the steady-state concentrations are of the order of 10^{-8} *M*. The average distance of separation of particles at this concentration is *ca.* 10^4 Å. The time required for a pair to reach such a displacement distance at moderate viscosity is of the order of 1×10^{-4} sec. The pair thus exists until another event such as recombination or some other reaction destroys one or both members.

The solution[9] for the diffusion equation for a finite cylindrical source is

$$P(x,t) = \frac{A}{4\rho}\left(\operatorname{erf}\frac{(\rho/2)+x}{\sqrt{4Dt}} + \operatorname{erf}\frac{(\rho/2)-x}{\sqrt{4Dt}}\right) \qquad (1)$$

where $P(x,t)$ is the probability in terms of distance (x) and time (t), A is a normalization constant, ρ is the collision diameter of the pair, and D is the effective diffusion coefficient for the pair. The form of eq 1 is shown in Figure 2.

The solution is expressed in the form of a probability since the experimental observations are the result of the behavior of many *independent* radical pairs. The probability function (1) gives unit probability that the pair exists within the interval $-\rho/2 < x < \rho/2$ at time zero. At the times greater than zero, there is a finite rising probability that the pair exists outside this interval. We define the pairs existing outside the original volume element ($|x| > \rho/2$) as the diffusively separated pair. The probability for this diffusive separation $[P_d(t)]$ is then the integral of (1) from $-\infty$ to $-\rho/2$ and $\rho/2$ to $+\infty$.

$$P_d(t) = \frac{\sqrt{4Dt}}{2\rho}\left[\frac{2}{\sqrt{\pi}} - 2i\operatorname{erf}c\left(\frac{\rho}{\sqrt{4Dt}}\right)\right] \qquad (2)$$

In addition to the destruction of the caged pair by diffusive separation (2), further reaction within the cage

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(1) J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.*, **89**, 6904 (1967).

(2) T. Koenig and M. Deinzer, *ibid.*, **90**, 7014 (1968).

(3) T. G. Traylor and H. Kiefer, *ibid.*, **89**, 6667 (1967).

(4) T. Koenig and M. Deinzer, *ibid.*, **88**, 4518 (1966).

(5) K. Smith and W. A. Pryor, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March–April 1968, p P-76.

(6) The connection between the rate and yield functions is that provided in ref 2.

$$\frac{1}{y} - 1 = \frac{k_o}{k_s} = \frac{1}{(k_1/k_o) - 1} = \frac{k_1}{k_s} - 1 = \frac{k_d}{k_c} + \frac{k_2}{k_c}$$

where y is yield of a cage product, k_1 is the rate constant for cleavage of the bond, k_o is the observed rate constant for over-all destruction of an initiator, k_s the observed rate constant for scrambling of label; k_d is the *formal* rate constant for diffusive separation, k_c is the rate constant for combination, and k_2 is the rate constant for any facile competing path (such as decarboxylation).

(7) R. M. Noyes, *Progr. Reaction Kinetics*, **1**, 131 (1961).

(8) W. Braun, L. Rajbenback, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1960).

(9) A. Stefan, *Sitzber. Akad. Wiss.*, [II], **68**, 385 (1873).

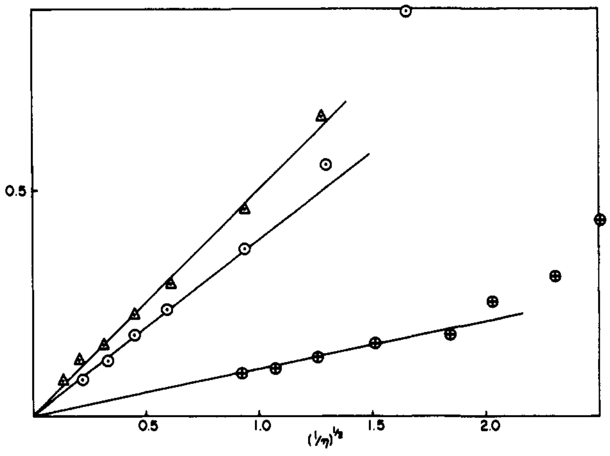

Figure 1. △ $(1/y_{ROOR}) - 1$, $(t\text{-BuOOC(=O)})_2$, ref 3 (expanded scale); ⊙ $(1/y_{ROOR}) - 1$, $(t\text{-BuON})_2$, ref 3 (expanded scale); ⊕ $1/[(k_1/k_o) - 1]$ $(n\text{-BuO})_2$, ref 5.

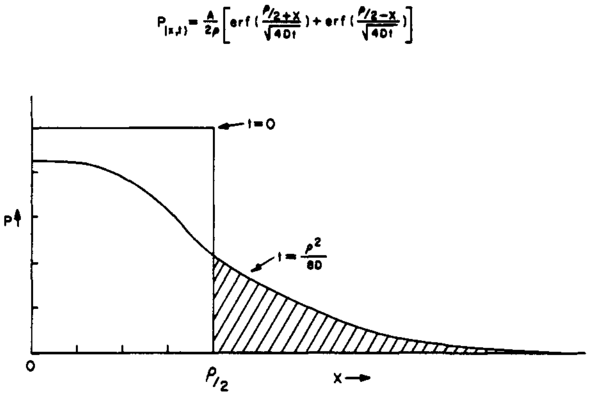

Figure 2. Probability density at $t = 0$ and $t = \rho^2/8D$.

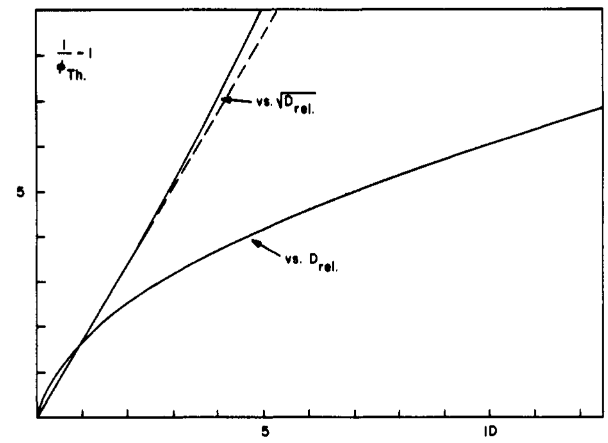

Figure 3. Calculated yield function *vs.* D_{rel} and $\sqrt{D_{rel}}$.

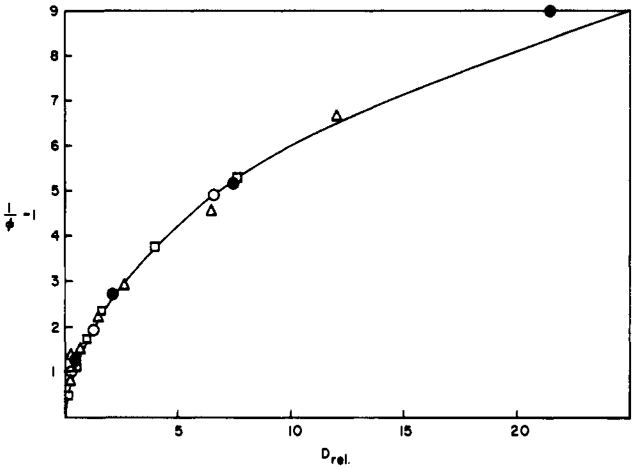

Figure 4. Fit of literature data to equation 7: ● $(1/y) - 1$, $C_6H_5CO_3\text{-}t\text{-Bu}$, ref 2 and 4; ○ $(1/y) - 1$, $CH_3O\text{-}t\text{-Bu}$, ref 2; △ $(1/y) - 1$, $(t\text{-BuO})_2$, ref 3; □ $(1/y) - 1$, $(t\text{-BuO})_2$, ref 3.

can occur by combination with a rate constant, k_c. Also, some other chemical reaction (given the general rate constant k_2) such as decarboxylation, hydrogen atom abstraction, β scission, or scavenging could conceivably compete. The probability that the caged pair exists at time t [$\theta(t)$] can be approximated as

$$\theta(t) = e^{-(k_2+k_c)t}[1 - P_d(t)] \tag{3}$$

The yield of cage combination product (φ) is the integral of $k_c\theta(t)\mathrm{d}t$ from zero to infinity (4).

$$\phi = \int_0^\infty k_c\theta(t)\mathrm{d}t \tag{4}$$

Expansion gives

$$\phi = \int_0^\infty k_c e^{-(k_c+k_2)t}\mathrm{d}t - \int_0^\infty \frac{4Dt}{\pi\rho^2} k_c e^{-(k_2+k_o)t}\mathrm{d}t + \int_0^\infty \sqrt{\frac{4Dt}{\pi\rho^2}} e^{-[(k_2+k_c)t-(\rho^2/4Dt)]}\mathrm{d}t - \int_0^\infty k_c e^{-(k_c+k_2)t} \operatorname{erf} c\left(\frac{\rho}{\sqrt{4Dt}}\right)\mathrm{d}t \tag{5}$$

The necessary integrals have been evaluated and the yield finally is given as eq 6.

$$\left(\frac{k_2 + k_c}{k_c}\right)\phi = 1 - \sqrt{\frac{D}{(k_2 + k_c)\rho^2}}\left(1 - e^{-\sqrt{(k_2+k_c)\rho^2/D}}\right) \tag{6}$$

The function which on an intuitive basis[2] should be simply related to fluidity is $(1/\phi) - 1$. Rearrangement of (6) to this form gives

$$\frac{1}{\phi} - 1 = \frac{k_2}{k_c} + \sqrt{\frac{D}{k_c\rho^2}}[1 + (k_2/k_c)] \times \left[\frac{1 - e^{-\sqrt{\rho^2(k_2+k_c)/D}}}{1 - \sqrt{\frac{D}{\rho^2(k_2 + k_c)}}\left(1 - e^{-\sqrt{\rho^2(k_2+k_c)/D}}\right)}\right] \tag{7}$$

Figure 3 shows this function (7) to be strongly curved when plotted vs. D_{rel} but very nearly linear with the square root of that quantity. Figure 4 shows a fit of some literature data to the calculated curve. The near linearity with $\sqrt{D_{rel}}$ is a result of the slow variation of the term on the right in brackets. If this variation is neglected by setting this term equal to a constant (β) then

(7) is formally identical with the simplistic model given

$$\frac{1}{\phi} - 1 = \frac{k_2}{k_c} + \sqrt{\frac{D}{k_c\rho^2}\left(1 + \frac{k_2}{k_c}\right)}\beta_{(\rho)} \qquad (8)$$

previously.[2] The equation can be interpreted in terms of simple slope intercept analyses as above.

The model predicts that only those radical pairs with facile alternative reactions $[k_2 \sim k_c]$ should have nonzero intercepts. It should be noted from Figure 3 that $1/(\phi - 1)$ could appear to be correlated with $1/\eta^{10,11}$ over a limited range of viscosity while actually following the present relationship. Extrapolation to infinite viscosity would give a positive intercept which would disappear if plotted *vs.* $\sqrt{1/\eta}$.

The factors which influence the slope of the approximately linear part of (7) are the size and molecular weight of the diffusing pair which determines the proportionality constant between D and $1/\eta$.[7] The time constant for combination also enters since this slope is related to the ratio of rates of diffusive displacement to combination. A positive intercept also raises the slope. This is because of the difference in the time dependence of the diffusive rate parameter (k_d) and that for chemical reaction. The effective or average rate constant for diffusive separation depends on the time interval over which it operates. For short times it is greater than for long times.

The combination diameter (ρ) also effects the magnitude of the slope in an important way. We have assumed this to be a property of the radical pair undergoing diffusion and not of the medium. This could be so if its value were related to the separation distance required for the pair to have escaped the long-range attractive part of the bonding potential. From this point of view, the classical potential energy of activation for the recombination step could be (though not necessarily) negative. The free energy of activation for recombination could still be positive because of the entropy changes on going from a radical pair to a single molecule.

A relative constancy in this parameter might also hold for solvents of varying viscosity if the variation in medium were due to solvent molecules of increasing chain length. The long molecules, while having over-all larger size, could still have one dimension which was fairly constant. The smallest dimension of a solvent molecule might determine ρ in the high viscosity region.

Most of the plots of $(1/\phi) - 1$ *vs.* $\sqrt{1/\eta}$ show strong upward curvature in the low-viscosity region. Low viscosity media are, of necessity, made up of small solvent molecules. This strong upward curvature could thus be rationalized as an indication of the range of viscosities over which a constant ρ will hold. Some upward curvature is predicted by the β term but it does not appear to be strong enough to account for the observed behavior.

Equation 7 is directly applicable to the combination behavior of primary radical pairs only (no intervening species such as nitrogen or carbon dioxide). The measured yield of combination products which must have had intervening molecules separating the geminate partners still appear to be correlated by a square-root dependence of fluidity. A volume element of height, ρ, can still be defined which contains such a pair. For the same formal species ρ may or may not be the same as ρ'. The displacement distance required for separation must be adjusted for the formation at partial separation by subtracting this initial distance (R_0). The effect of the intervening molecule on combination is taken into the empirical value of k_0. Equation 6 should be modified by replacing ρ with $\rho - R_0$.

Data of ref 2 demonstrate that there is a significant reduction in the probability of recombination of acetoxy–*t*-butoxy radical pairs generated from the corresponding hyponitrite compared to those from *t*-butyl peracetate.

$$\frac{1}{\phi} - 1 = \frac{k_2}{k_c} + \sqrt{\frac{D}{k_c(\rho' - R_0)}\left(1 + \frac{k_2}{k_c}\right)}\beta_{(\rho' - R_0)} \qquad (9)$$

The higher observed slopes[2] of the yield–square-root fluidity correlations for radical pairs generated with intervening molecules compared to those observed for the same formal pair without an intervening molecule (Figure 1) can thus be explained in two ways. The increase could be due either to a reduction in the diffusive displacement distance required for separation of the pair $[(\rho' - R_0) < \rho]$ or due to a reduction in k_c for the molecule separated compared to the unseparated pair. The magnitude of these slope ratios appears to be of the order of 10^2 which seems to be somewhat larger than expected for $\rho/(\rho' - R_0)$. We therefore have favored[2] the latter explanation as being at least the major contributor to this increase.

This model makes the seemingly drastic assumption that once displacement beyond a distinct distance $(\rho' - R_0)$ has occurred, there is no longer any chance of recombination. This is only formally true since the experimental observations reflect only the effective or average values of $\rho' - R_0$ and k_c. The value of $\rho' - R_0$ is dependent to some extent on the reactivity of the radicals in question. For inert radical pairs like iodine atoms,[12] some of the primary pairs could escape recombination and reach a solvent-separated state. A new volume element of height, ρ'', can still be defined which contains these pairs. Also a new rate constant k_c' can be defined which takes into account the reduced probability that they may recombine. Considerable recombination of such pairs might be expected since they can do little else.

A case in contrast is the acetoxy radical pairs generated in the decomposition of acetyl peroxide. Here, decarboxylation is expected to occur at a rate comparable with cage recombination. Figure 5 shows plots of the functions of the over-all rate[8] of decomposition of the peroxide and the rate of scrambling of the oxygen atom[13] which should correspond to $1/(\phi - 1)$. Both cases show positive intercepts which, according to (8) are $2k_2/k_c$.

Those pairs which have reached a diffusive displacement with respect to primary recombination will not contribute much to the reformation of the peroxide if solvent separation has occurred. This statement is made because the mere presence of a nitrogen molecule

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[10] S. Szwarc, K. Chakravorty, and J. M. Pearson. *J. Am. Chem. Soc.*, **89**, 283 (1967).

[11] K. Smith and W. A. Pryor, *ibid.*, **89**, 1741 (1967).

[12] R. M. Noyes and D. Booth, *J. Am. Chem. Soc.*, **82**, 1868 (1960).

[13] J. C. Martin and S. Dombchick, "Oxidation of Organic Compounds—I," Advances in Chemistry Series No. 75, American Chemical Society, Washington, D. C., 1968, p 269.

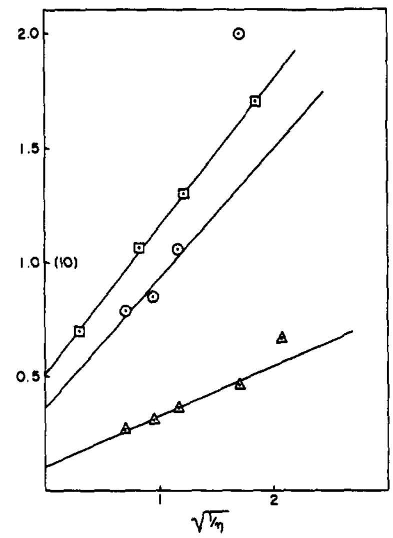

Figure 5. ☐ $(k_1/k_c) - 1$, Ac_2O_2, ref 13 ($k_1 = k_{gas}$, ref 16); ⊙ $1/[(k_1/k_o) - 1]$, Ac_2O_2, ref 8 ($k_1 = k_{gas}$, ref 16); △ $1/(Y - 1)$, $CH_3CO_2CH_3$, ref 8 (expanded scale).

appears to reduce the combination probability by 10^2. The decarboxylation of the primary pairs is already comparable to their combination rate. Thus the high reactivity of the radical pair can effect the displacement distance over which recombination is averaged.

A more subtle consequence arises when one considers the fates of the methyl–acetoxy pairs formed in the primary cage and after diffusive displacement with respect to primary acetoxy–acetoxy recombination. The pairs which have diffused from primary reaction need not be excluded from contributing to cage formation of methyl acetate. The primary pairs which decarboxylate give methyl–acetoxy radical pairs separated by a carbon dioxide. These may not have such different combination rates from the methyl–acetoxy radical pairs formed by one decarboxylation of the acetoxy–acetoxy pairs which have undergone diffusive separation. The combination rates of methyl–acetoxy pairs could be significantly greater than acetoxy–acetoxy pairs at all separation.

Some support of this position is already available. The intercepts of the rate function plot for acetyl peroxide (Figure 5) is about one-fifth that for the yield function for methyl acetate (Figure 5). This is a significantly smaller difference than that observed for the slopes of the rate function for di-*n*-butyl peroxide compared to that for the yield of di-*t*-butyl peroxide from the hyponitrite (Figure 1). An increased efficiency of combination involving methyl radicals could partly compensate for the formation of the radical pairs with a carbon dioxide molecule intervening. These considerations provide a rationalization for neglecting the fraction of pairs which have diffused from a prior combination reaction from subsequent combination–diffusion competitions.

Similar arguments apply to the formation of ethane from the peroxide. The dimensions of the volume element (ρ) required to encompass all of the methyl–acetoxy and methyl–methyl pairs, which are generated sequentially from discreet previous intermediates, should be a function of viscosity. However, R_0 is determined by a similar dependence and the value of $\rho' - R_0$ could remain relatively constant.

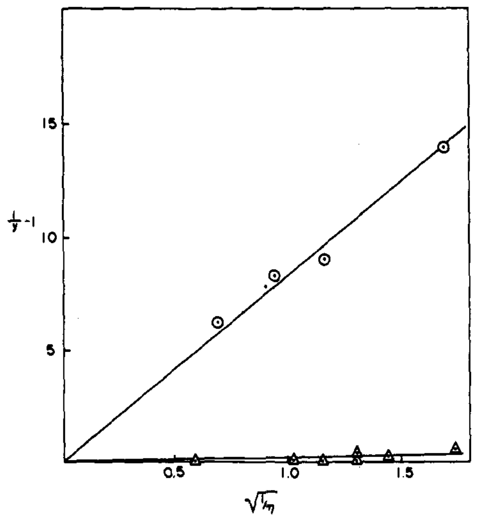

Figure 6. ⊙ $[(1 - y_{CH_3CO_2CH_3})/y_{CH_3CH_3}] - 1$, Ac_2O_2, ref 8; △ $(1/y_{CH_3CH_3}) - 1$, $(CH_3N)_2$, ref 10.

The slope of the ethane yield correlation from the decomposition of acetyl peroxide is quite high while that from the photolysis of azomethane is low (Figure 6). Within the present framework, this difference could be rationalized as being due to the difference in the distance of separation when the methyl–methyl radical pairs are formed and its effect on k_c. In the former case, two carbon dioxides and some solvent molecule(s) probably intervene (in fluid media) by the time both acetoxy radicals have decarboxylated. The combination rate (k_c) would, therefore, be expected to be reduced by a large factor compared to that for primary pairs of the same type. The azomethane photolyses would be expected to give methyl–methyl pairs which would have larger combination probabilities though perhaps still not as large as the primary species (without an intervening nitrogen molecule). Considering the effect of a nitrogen molecule on oxy–oxy recombination,[2] the slope of the yield function for recombination of methyl–methyl pairs generated with no interveing molecule might be very small indeed.

One of the most valuable quantities which result from the present treatment is the intercept which is obtained for a species which can undergo some reaction, in addition to diffusion, at a rate comparable to that for combination. The correlations derived from the present treatment for the decomposition of acetyl peroxide give a significantly altered picture for the process from that proposed by other workers. The ratio k_2/k_{-1}, obtained from the intercept of the plot (Figure 5) is *ca.* 0.25. This value indicates that, in isooctane at 80°, 37% of the acetoxy–acetoxy radical pairs return, 16% decarboxylate as primary cage pairs and the remainder undergo diffusive displacement. At infinite viscosity, 67% of the pairs would return and 33% would decarboxylate (at this temperature).

This type of analysis is necessary before any interpretation of isotope effects (deuterium[14] or heavy atom[15]) on this reaction can be put forth since a single rate-

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(14) T. Koenig and W. D. Brewer, *Tetrahedron Letters*, 2773 (1965).
(15) M. J. Goldstein, *ibid.*, 1601 (1964).

determining step cannot be defined. Any theoretical model for a single transition state[15] for such reactions will give unrealistic results unless proper account is taken of the composite nature of the over-all process. The present model is proposed as a way of adjusting for this situation. Another valuable property of the intercepts is their temperature dependence. If rates of oxygen atom scrambling and destruction of acetyl peroxide as well as yield data for methyl acetate were available at several temperatures, and several viscosities, then $\Delta\Delta E_a$ for k_2/k_{-1} could be obtained. The $(\Delta\Delta E_a)$ would then reflect the difference in activation energies for the two combination (k_{-1}) processes since decarboxylation (k_2) of the same species is involved in each case.

The main purpose of this paper is to suggest a formalism, which at this point is very crude, with the hope that it can be tested as well as refined. We have purposely exercised some license in providing rationalizations of the existing data in terms of the present model, as if it were a proven theory. These rationalizations suggest the types of refinements which should be looked at. The distribution of k_c and ρ as functions of viscosity contain much useful information. They might ultimately give an explanation for the upward curvature in the high fluidity range which is observed with the present as well as with previous models. Tests of the present model should also be carried out. For example, the rationalization of high slope in the ethane yields from acetyl peroxide suggests that a reactive enough scavenger, present in modest concentration, should be capable of interfering with the ethane formation. Existing data[16] suggests this prediction is incorrect but reinvestigation with other scavengers seems justified. The predictions of the present model with respect to scavange ability of radical pairs are currently being analyzed.

Acknowledgment. We are grateful for the financial support of the National Science Foundation and Professor R. M. Mazo for helpful discussion of this work.

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[16] M. Szwarc, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., John Wiley & Sons, Inc., New York, N. Y., 1962, pp 153–174.

Secondary Deuterium Isotope Effects in Radical-Forming Reactions. III. The Decomposition of Acetyl Peroxide

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Abstract: The α-deuterium secondary kinetic isotope effect on the decarboxylation of the acetoxy radical has been estimated from the ratio of yields of the two isomeric trideuterated methyl acetates formed from decomposition of unsymmetrically trideuterated acetyl peroxide. The estimated isotope effect is 1.09 ± 0.02 for three deuterium atoms. The isotope effects on the over-all decomposition rates have been measured by a new double-labeling technique. These isotope effects are small and appear to be sensitive to changes in temperature and solvent viscosity. They are interpreted in terms of a mechanism in which diffusive separation of the acetoxy–acetoxy radical pair is included.

Our initial interest[1] in secondary deuterium isotope effects in peroxide decompositions arose indirectly from the observation of apparent exchange between the carbon dioxide forming intermediates in the decomposition of labeled acetyl peroxide and added unlabeled acetate ion.[2] Our interpretation of these observations was that the acetoxy radical intermediate produced in the process had a sufficient lifetime to undergo electron exchange with the acetate ion present. Just after the preliminary electron exchange results were first obtained, a report of a study of the heavy atom isotope effects on the decomposition of this peroxide was published.[3] The conclusion from this study was that this reaction was a "concerted" process involving C–C as well as O–O bond breaking. We thus felt that the deuterium isotope effect should be examined as a method for choosing between these apparently different conclusions as to the mechanism of the decomposition. Initial isotope effect studies, carried out using conventional kinetic techniques, indicated that there was very little if any effect of deuteration on the rate of decomposition of this peroxide; a result which was apparently in accord with expectations for a stepwise mechanism with the intervention of a well-defined acetoxy radical intermediate.

Relatively few radical reactions have been investigated using secondary isotope effects and so we felt it was worthwhile to continue this line of endeavor and examine the isotope effect on the decarboxylation process. It had previously been shown[4] that the methyl acetate product was probably a result of a cage reaction. Thus an estimate of this isotope effect appeared accessible from the determination of the ratio of yields of the two trideuterated methyl acetates which could be formed from the trideuterated peroxide. The results of these experiments are detailed below.

During the course of this work, it was elegantly demonstrated[5] that the decomposition of acetyl peroxide involves the *reversible* formation of acetoxy radicals

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[1] W. D. Brewer and T. Koenig, *Tetrahedron Letters*, 2773 (1965).

[2] W. D. Brewer, unpublished results in these laboratories; T. Koenig and R. Wielesek, submitted for publication.

[3] M. Goldstein, *Tetrahedron Letters*, 1601 (1964).

[4] L. Herk, M. Feld, and S. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).