Secondary Deuterium Isotope Effects in Radical-Forming Reactions. V. *t*-Butyl Peracetate and Substituted *t*-Butyl Phenylperacetates

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Abstract: The secondary deuterium isotope effects on the thermal decomposition of *t*-butyl peracetate (**6**), *t*-butyl *p*-nitrophenylperacetate (**7**), and *t*-butyl *p*-methoxyphenylperacetate (**8**) have been measured. The isotope effect for compound **6** is very small ($k_{\mathrm{H}}/k_{\mathrm{D}} = 1.00 \pm 0.02$ in isooctane at 130.10°). The isotope effect on the decomposition of **7** is 1.10 for two deuteriums at 85° in chlorobenzene and 1.09 at the same temperature in Nujol. Compound **8** has an isotope effect of 1.07 for two deuteriums in isooctane at 60.4°, and at the same temperature in Nujol the effect is found to be 1.05. The very small isotope effect for **6** is interpreted in terms of a nonconcerted decomposition, while the larger effects observed for **7** and **8** are compared to that observed in the case of *t*-butyl phenylperacetate. A study of oxygen-18 scrambling in the decomposition of **6** is discussed in terms of possible mechanistic refinements for perester decompositions.

The thermal decomposition of peresters has been thought of as proceeding by two possible mechanistic routes:[1,2] a "concerted" pathway in which carbon–carbon and oxygen–oxygen bonds break simultaneously forming carbon dioxide and radical fragments, and a "nonconcerted" decomposition in which an acyloxy radical is a discrete intermediate.

Bartlett,[3] in his studies on the decomposition of various substituted *t*-butyl phenylperacetates, found that their rates could be correlated moderately well with σ^+ to give ρ −1.09. A relatively large degree of charge separation in the transition state seems indicated by the magnitude of this reaction constant.

Pryor[4] has recently questioned this interpretation of the data for these compounds. Noting the viscosity dependence of the decomposition rate and using a σ–ρ treatment, he has suggested that some members of the series, notably the *p*-nitro and unsubstituted compound, may decompose in part by the nonconcerted route.

Work has been reported from these laboratories[2,5] concerning secondary deuterium isotope effects on the decomposition of compounds **1–5**. The β effects observed for compounds **1**, **2**, and **3** were

$$\underset{\mathbf{1}}{(CH_3)_3CO_3C(CH_3)_3} \quad \underset{\mathbf{2}}{C_6H_5C(CH_3)_2CO_3C(CH_3)_3}$$

$$\underset{\mathbf{3}}{C_6H_5CH(CH_3)CO_3C(CH_3)_3}$$

$$\underset{\mathbf{4}}{(CH_3CO_2)_2} \quad \underset{\mathbf{5}}{C_6H_5CH_2CO_3C(CH_3)_3}$$

small (1.014–1.020 per deuterium) but considered "normal" for a radical-forming reaction.[1,5] The α effects in the case of **3** and **5** were lower (1.03–1.06 per deuterium) than had been expected on the basis of isotope effects previously observed for the decomposition of azo compounds.[6] They were, however, significantly greater than the corresponding isotope effects measured for the decomposition of acetyl peroxide (**4**), which appears to be unquestionably nonconcerted.[2] Thus the effects for **3** and **5** were interpreted in terms of a concerted process.[2a]

This paper is a report of studies made on three more peresters: *t*-butyl peracetate (**6**), *t*-butyl *p*-nitrophenylperacetate (**7**), and *t*-butyl *p*-methoxyphenylperacetate (**8**). It was hoped that **7** and **8** would

$$\underset{\mathbf{6}}{CH_3CO_3\text{-}t\text{-}Bu} \quad \underset{\mathbf{7}}{p\text{-}NO_2C_6H_4CH_2CO_3\text{-}t\text{-}Bu}$$

$$\underset{\mathbf{8}}{p\text{-}MeOC_6H_4CH_2CO_3\text{-}t\text{-}Bu}$$

provide greater understanding of the isotope effect previously obtained for *t*-butyl phenylperacetate, and that **6** would provide a clear case of a nonconcerted perester decomposition.

Results

Isotope effects for the decompositions of **7** and **8** were obtained by two methods: infrared determination of the rate constants for both deuterated and undeuterated perester, and a competitive double-labeling experiment in which a mixture of deuterated and undeuterated perester labeled in the carbonyl position with oxygen-18 are decomposed and the oxygen-18-enriched carbon dioxide produced is analyzed by means of a mass spectrometer at infinite and short times. Both techniques have been previously described.[1,2]

In the double-labeling experiments the carbon dioxide from the reaction was collected on a vacuum line and shown to be free of interfering impurities. Isooctane was detectable in the mass spectra but it had been shown not to interfere with the measurements.[2] The isotope effect is obtained from the m/e 46/44 ratios by means of expression 1.[2] Here R_0^{m}, R_0^{d}, and R_0^* are the ratios obtained from samples of carbon dioxide collected after short reaction time from a mixture of oxygen-18-enriched and deuterated perester, pure deuterated perester, and pure oxygen-18-enriched perester, respectively, and R_∞^{m}, R_∞^{d}, and R_∞^* are the

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(1) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

(2) (a) T. Koenig and R. Wolf, *ibid.*, **91**, 2575 (1969); (b) T. Koenig and R. Cruthoff, *ibid.*, **91**, 2562 (1969).

(3) P. D. Bartlett, and C. Ruchardt, *ibid.*, **82**, 1762 (1960).

(4) W. A. Pryor and K. Smith, Abstracts of Papers, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, ORGN-113.

(5) T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **91**, 2569 (1969).

(6) S. Seltzer and E. Hamilton, *ibid.*, **88**, 3775 (1966).

Table I. Infrared Kinetic Results[a] for **7** and **8**

Compd	Solvent	Temp, °C	$k_0 \times 10^4$, sec^{-1}	$k_0' \times 10^4$, sec^{-1}	k_0/k_0'
7	Chlorobenzene	85.10	0.370	0.340	1.10
7	Chlorobenzene	85.10	0.385	0.355	1.09
8	Isooctane	60.46	0.472	0.453	1.07
8	Paraffin oil[b]	60.46	0.420		

[a] From linear least squares analysis. [b] Paraffin oil and Nujol have been found to have identical viscosity behavior.

Table II. Double Labeling Results[a] for **6**, **7**, and **8**

Compd	Solvent	T, °C	R_0^{M}	R_0^{D}	R_0*	R_∞^{M}	R_∞^{D}	R_∞*	k_0/k_0' [b]	(k_{16}/k_{18})* [c]	(k_{16}/k_{18})D[d]	n/n* [e]
6	Isooctane	130.1	1.842	0.534	3.110	1.892	0.551	3.188	1.00	1.025	1.030	1.017
6	Oil	130.1	1.845	0.530	3.106	1.889	0.549	3.196	1.02	1.028	1.035	1.024
7	Oil	84.98	2.034	0.408	3.596	2.039	0.4099	3.707	1.066	1.031	1.004	0.976
7	Oil	84.98	2.043	0.409	3.574	2.011	0.414	3.699	1.129	1.035	1.010	0.946
8	Isooctane	60.46	1.711	0.495	2.887	1.702	0.496	2.933	1.056	1.016	1.002	0.958
8	Isooctane	60.46	1.722	0.492	2.887	1.705	0.498	2.937	1.078	1.018	1.015	0.960
8	Oil	60.46	1.715	0.493	2.868	1.710	0.499	2.913	1.053	1.016	1.013	1.009
8	Oil	60.46	1.714	0.493	2.885	1.709	0.496	2.924	1.043	1.013	1.007	1.002

[a] R indicates 46/44 mass spectral peak intensity ratios × 100. [b] Apparent total overall isotope effect, eq 1. [c] Apparent oxygen-18 isotope effect from labeled compound. [d] Apparent oxygen-18 isotope effect from unlabeled compound. [e] Ratio of yields of carbon dioxide from labeled and unlabeled compound.

corresponding ratios measured for samples collected after "infinite" reaction time (greater than six half-lives). The expression allows calculation of n^*/n, the number of moles of enriched carbon dioxide liberated per mole of carbon dioxide liberated from the deuterated compound. This ratio should be nearly unity if both peresters are equally pure. The apparent oxygen-18 effects can also be obtained

$$\frac{k_0}{k_0'} = \frac{(R_0^{\mathrm{m}} - R_0^{\mathrm{d}})(R_\infty^* - R_\infty^{\mathrm{m}})}{(R_\infty^{\mathrm{m}} - R_\infty^{\mathrm{d}})(R_0^* - R_0^{\mathrm{m}})} \qquad (1)$$

where k_0 and k_0' are the rate constants for overall decomposition of the protio and deuterio compound, respectively.

In the case of the *p*-methoxy and *p*-nitro compounds, runs were made using solution *ca.* 0.05 *M* in perester and 0.1 *M* in styrene to inhibit induced decomposition. The results of the infrared studies for the *p*-nitro (**7**) and *p*-methoxy (**8**) compounds are shown in Table I, and the double-labeling results for all three compounds are shown in Table II.

The *p*-nitro perester (**7**) presented certain experimental difficulties in these studies The solubility of the material in isooctane and oil was low at room temperature and below; hence its infrared kinetics in these solvents could not be obtained with the available equipment At temperatures nearing those used for its decomposition, however, it became soluble in these solvents, making it possible to attempt the double-labeling studies. But in isooctane the apparent oxygen-18 isotope effects for the enriched perester were inverse and nonreproducible, indicating some loss of oxygen-18 through a side process in this solvent. In such cases the data obtained by this method are useless. This problem did not arise in Nujol, but the difficulty in preparing accurate, homogeneous solutions of the compound lowers the precision of the results. The average of the data shown in Table II gives $k_0/k_0' = 1.09 \pm 0.03$. The n^*/n ratio was near unity and the oxygen-18 isotope effects were similar to those observed for *t*-butyl phenylperacetate[2a] The infrared kinetics could be obtained in chlorobenzene, and by this technique it was found that $k_0/k_0' = 1.10$.

No such experimental difficulties were encountered in experiments with *t*-butyl *p*-methoxyphenylperacetate (**8**), it being sufficiently soluble to allow both infrared and double-labeling studies to be done in isooctane and oil. The isotope effect observed in isooctane by the double-labeling technique was the same as that obtained in the same solvent by the infrared method ($k_0/k_0' = 1.07$ for two deuteriums). The rate constant observed in oil was slightly lower than in isooctane but the isotope effect estimated by the double-labeling method was slightly smaller in Nujol ($k_0/k_0' = 1.05$). In all cases n^*/n was near unity and the oxygen-18 isotope effects were of the magnitude expected.

Rates of decomposition of *t*-butyl peracetate (Table III) were measured by the infrared method with and without added iodine in solvents of varying viscosity. Iodine had a negligible effect suggesting induced decomposition is unimportant in these solvents. The rates were definitely affected by the viscosity variation[4] as is expected for a nonconcerted reaction. No attempt was made in this case to estimate the isotope effect by the infrared method because of the small value expected. The double-labeling results verified this expectation.

Table III. Infrared Rate Constants[a] for Decomposition of **6** at 130.1°

Inhibitor	Hexane	60% hexane	30% hexane	Oil
None	5.17	4.39	4.11	3.21
None	4.93	4.47	3.86	3.04
0.3 *M* I_2	5.01		3.72	
0.3 *M* I_2	5.21		3.92	
Av	5.08	4.43	3.80	3.13
$\eta_{130°}$, cP	0.140	0.378	0.820	2.44

[a] Linear least squares rate constants × 10^4 sec^{-1}.

An attempt was also made to measure the rate constant of scrambling of carbonyl oxygen-18 labeled **6** as a function of viscosity. The analytical method was the methoxide cleavage sequence published in connection with studies of the corresponding nitroso hydroxylamine.[7] The results are summarized in Table

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(7) T. Koenig and M. Deinzer, *J. Amer. Chem. Soc.*, **90**, 7014 (1968); in press.

Table IV. Estimated Rate Constants for Oxygen-18 Scrambling of Carbonyl Labeled **6** at 130.1°

Solvent	46/44 direct[a]	46/44 *p*-nitroperbenzoate[b]	t, min	$k_s \times 10^4$, sec^{-1} [c]
Hexane	3.110	0.406	8.0	
Hexane	3.174	0.556	23.0	1.31
60% hexane	3.124	0.446	8.4	
60% hexane	3.178	0.630	26.0	1.66
Paraffin oil	3.113	0.469	11.9	
Paraffin oil	3.163	0.801	39.2	2.08

[a] The 46/44 mass spectral ratios (× 100) from the carbon dioxide formed from labeled **6** after the times indicated. [b] The 46/44 mass spectral ratios (× 100) from *t*-butyl *p*-nitroperbenzoate obtained from the *t*-butoxy fragment[7] from *t*-butyl peracetate recovered after the times indicated. [c] Calculated by the difference in ln [1/(1 − fraction equilibrated)].

IV. The values of k_s were obtained from the difference in the fractions equilibration' at the two times rather than from a normal first-order appearance plot. Such three-point (including 0 time) first-order plots were found to show strong upward curvature. This was subsequently found to be a result of the relatively long time (approximately 5 min) required for the large volumes of solution needed in these runs to approach the temperature of the bath. Using the two-point difference corrects for most of this temperature induction period. More accurate methods for these determinations are being investigated presently but the semiquantitative results appear to be precise enough to warrant discussion.

Discussion

Isotope Effects. The qualitative observations of relatively strong sensitivity of k_0 for **6** to viscosity and the fact that recovered perester after part decomposition was scrambled are both indicative of a nonconcerted mechanism. The very small isotope effect on the k_0 ($k_0/k_0' = 1.00 \pm 0.02$ at both high and low viscosity) is also in qualitative accord with intuitive expectations for such a mechanism if the decarboxylation step does not contribute much to the overall rate in the forward direction.

The isotope effect observed for the decomposition of compound **8** is significantly lower than that observed in the case of the unsubstituted compound (**5**). However, it is still much larger than that measured for acetyl peroxide and *t*-butyl peracetate. The small decrease in the rate constant for the compound with the large change in viscosity in going from isooctane solvent to Nujol solvent might be taken as an indication of some contribution of a reversible nonconcerted pathway. The magnitude of this decrease is much smaller than that reported for **7** or **5** while the isotope effect for **8** is smallest of all three. Hence, this low α effect is difficult to explain by invoking a contribution from a competing nonconcerted process.

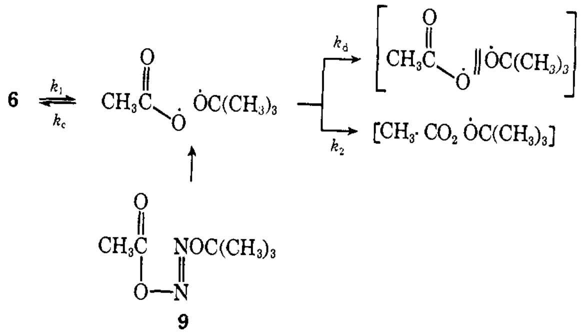
Previously the low isotope effect observed for the reaction of the phenylacetyl perester (**5**) was rationalized by a transition state in which the change in bending motion of the α-hydrogen atoms is reduced because of the developing carbon dioxide molecule in close proximity to the incipient radical pair.[2a] Activation volumes measured for peresters undergoing two-bond homolysis are small, lending some support to the rationalization.[8,9] It is interesting to note in this connection that in both the decomposition of the *p*-methoxyphenylperacetate and the unsubstituted phenylperacetate, a slightly lower isotope effect was observed in oil than in isooctane. If the more viscous solvent acts so as to compress the transition state, then a smaller isotope effect would be expected by this reasoning.

Another factor which could make an important contribution to the magnitude of the isotope effects for the series of substituted *t*-butyl phenylperacetates is the inductive effect. The greater electropositivity of deuterium as compared to hydrogen has been demonstrated by a decrease in acid dissociation constants for acetic, propionic, and phenylacetic acids upon deuteration in the α position.[10] The large negative ρ value observed by Bartlett for the phenylperacetate decompositions appears to indicate a significant degree of positive charge character at the α carbon in the transition state. Electron-releasing substituents such as *p*-methoxy would stabilize such a dipolar transition state and the inductive effect of the deuteriums would likewise increase the rate of the deuterio compound compared to that of the protio compound, thus decreasing the total isotope effect. The observed isotope effects of 1.07 for the *p*-methoxy compound and 1.12 for **5** are in the order expected by this rationalization if it is assumed that the transition states have the proper charge variation.

Extrapolation of this reasoning to the *p*-nitro compound would lead to the prediction of an increase in the magnitude of the isotope effect as compared to the others. Although data for the decomposition of the *p*-nitrophenylperacetate are admittedly not extremely precise, it does seem clear that the isotope effect is not much larger than that for the unsubstituted phenylperacetate. Pryor[4] has estimated, from the changes in rate with viscosity and *ad hoc* treatment of the σ–ρ behavior, that this compound undergoes 21% return from the cage in octane at 80°. The low value of the isotope effect in this case might be considered an additional indication of partial nonconcerted decomposition. Unfortunately, experimental difficulties have thus far frustrated our efforts to measure return in this compound directly by the type of oxygen-18 scrambling study done on the *t*-butyl peracetate.

***t*-Butyl Peracetate Combination Competition. Variable k_1.** The formalism which we have used to account for rate and product variations with viscosity changes when the nonconcerted mechanism is operative is summarized, for the present case, as Scheme I. Here, k_1

Scheme I



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(8) R. Neuman and J. Behar, *J. Amer. Chem. Soc.*, **89**, 4549 (1967).

(9) R. Neuman and J. Behar, *Tetrahedron Lett.*, 3281 (1968).

(10) E. A. Halevi, M. Nussin, and A. Ron, *J. Chem. Soc.*, 866 (1963).

Table V. Summary of Viscosity Effects on Decomposition of **6** at 130.1°

Solvent[a]	$(1/\eta)^{1/2}$	$k_0 \times 10^4$, sec^{-1}	$k_s \times 10^4$, sec^{-1}	k_0/k_s	$k_1 \times 10^4$, sec^{-1}	f_s[b]
Hexane	2.64	5.08	1.31	3.89	6.39	1.00
60% hexane	1.63	4.43	1.66	2.56	6.09	0.84
30% hexane	1.10	3.80	(1.93)[c]	(2.05)[c]	5.73	0.79
Paraffin oil	0.64	3.13	2.08	1.54	5.21	0.65

[a] Hexane–paraffin oil mixtures. [b] $k_s/(6.39 - k_0)$. [c] Taken from Figure 3.

is the first-order rate constant for homolysis of the O–O bond, k_c is the average rate constant for combination, k_d is the *effective rate constant* for diffusive separation of the pair, and k_2 is the first-order rate constant for decarboxylation of the acetoxy radical. These parameters are related to the experimentally accessible rate constant for overall disappearance of peroxide (k_0) and the rate constant for scrambling of carbonyl label (k_s) through (2). We have recently

$$\frac{1}{(k_1/k_0 - 1)} = \frac{k_1}{k_s} - 1 = \frac{k_0}{k_s} = \frac{k_2}{k_c} + \frac{k_d}{k_c} \qquad (2)$$

proposed[11] a simple model for the quantitative treatment of such competitions which assumes that the only viscosity-sensitive rate parameter is k_d which was shown to be related to the square root of fluidity. Pryor and Smith[4,12] have proposed a method of analysis which amounts to a reciprocal of the relationships of a square root viscosity dependence for diffusive displacement. The data of Table V allow tests of these relationships which are equivalent for the special case when $k_2/k_c \sim 0$ and k_d is the only viscosity-dependent rate parameter.

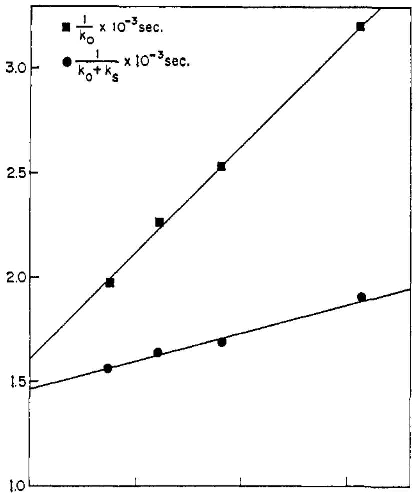

Figure 1. Viscosity variation in $1/k_0$ and $1/(k_0 + k_s)$.

The first and second functions in (2) require knowledge of k_1. The value of this rate constant should be the sum of $k_0 + k_s$ if it is *assumed* that every recombination leads to scrambling. An alternative is to use the method of Pryor and Smith and estimate k_1 from the intercept of a plot of $1/k_0$. Such a plot is shown in Figure 1. The value of k_1 is very close to the value obtained from the $k_0 + k_s$ in hexane.

Figure 2 is the composite plot of the three functions on the left in (2), the first two of which depend on the value of k_1. This figure demonstrates graphically the same information contained in Table V from the sums of k_0 and k_s, *i.e.*, that k_1 is not independent of viscosity. The importance of this small variation of k_1 with viscosity is most significantly demonstrated by the intercept variation which should be related to k_2/k_c in our[11] formalism. Using a single value for k_1 and the k_0 dependence alone gives a negligible intercept indicating that decarboxylation of the acetoxy radical is too slow to compete with combination of the unseparated pair. This is in strong contrast to the large intercept of the perester yield fluidity plot for the decomposition of the corresponding hyponitrite (**9**).[7] The scrambling data indicate that decarboxylation of the unseparated pair can compete with its combination. The k_0/k_s ratios do not depend on k_1, so that any variation in this parameter is not counted.

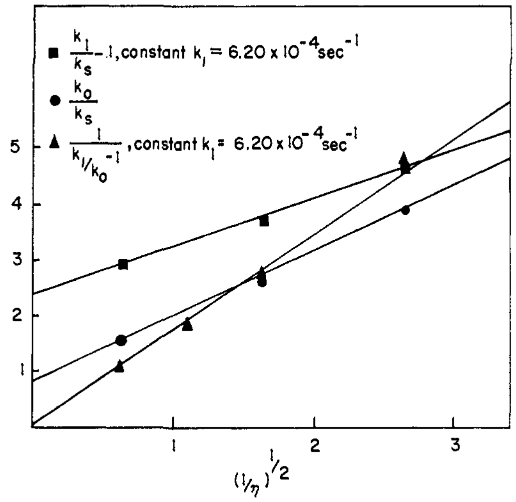

Figure 2. Fluidity correlations of eq 2 with constant k_1 = 6.20 × 10^{-4} sec^{-1}.

Figure 3 shows the comparison plot of the functions given in (2) using the variable k_1's. The line is equivalent to the k_0/k_s variation of Figure 2 which is independent of k_1. The intercept is *ca.* 0.8 and is interpreted as the ratio of k_2/k_c at 130°. This value can be compared with the value (0.25) estimated[11] at 80° from the oxygen-18 scrambling of acetyl[13] peroxide. The magnitude of the change is quite close to that predicted by the activation parameters for decarboxyla-

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(11) T. Koenig, *J. Amer. Chem. Soc.*, **91**, 2558 (1969).

(12) W. A. Pryor and K. Smith, Abstracts of Papers, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, P 76.

(13) J. C. Martin and S. M. Dombchick *Advan. Chem. Ser.*, No. 75, 269 (1967).

tion of the acetoxy radical estimated by Eirich[14] ($k_2^{130°}/k_2^{80°} = 3.2$).

A nonzero intercept is required for any of the isotope effect on the decarboxylation step to show up in the overall rate constant. Using the same method as described for acetyl peroxide[2] and the values of the slope and intercept of Figure 3 together with the measured[2] isotope effect on the decarboxylation of the acetoxy species ($k/k' = 1.09$ for three deuterium atoms at 75°, *uncorrected* for temperature change), the predicted k_0/k_0' ratios for the peracetate (**6**) are 1.025 in paraffin oil and 1.005 in isooctane. The observed values (1.00 and 1.02, respectively) do not appear to show the predicted increase with increasing viscosity. However, it should be emphasized that the uncertainties in these k_0/k_0' values are significantly larger than those reported for the acetyl peroxide case since the measurements were made on the carbon dioxide samples without purification. The small values anticipated (smaller than those calculated when temperature correction for the decarboxylation (k_2) isotope effect is made) discouraged the further work required to obtain the accuracy in the k_0/k_0' values sufficient to reflect a small increase with increasing viscosity. The distinction between concerted and nonconcerted behavior seems demonstrated clearly enough by the differences in k_0/k_0' values of **6** compared with the *p*-nitro and *p*-methoxy compounds (**7** and **8**).

The major conclusion which emerges from this possible rationalization of the discrepancies depicted by Figure 2 is that k_1 (the first-order rate constant for O–O bond homolysis) can show viscosity variation independent of subsequent diffusive steps. This means that small variations in k_0 for compounds such as **5** or **8** may merely be a reflection of the same type of behavior for the k associated with a concerted decomposition event. Figure 1 has included a plot of $1/(k_0 + k_s)$ observed for the peracetates (**6**) for comparison. The magnitude of the slopes of the $1/k_0$ plots for **5** and **8** are similar to this $1/(k_0 + k_s)$ variation. However, the *magnitude* of the variation in $1/k_0$ for **7** is similar to that of **6** (rather than $1/(k_0 + k_s)$). The *magnitudes* of the viscosity variations and the isotope effects as well must be analyzed since neither criterion gvies an unambiguous test for concerted *vs.* nonconcerted pathway. The trends in these magnitudes for the phenylacetyl series both suggest that some (partial) change in mechanism may be occurring as one goes from the *p*-methoxy to the *p*-nitro compounds although neither trend *demands* this conclusion.

Constant k_1-Variable Randomization. There is an alternative way to rationalize the contradictions of Figure 2 which puts the emphasis differently. The assumption of the above argument was that all combination events necessarily occur with scrambling of label. If one allows the possibility of recombination with retention of the label then a constancy in k_1 value at all viscosities can still be accommodated by the data. This would then mean that the $1/(k_1/k_0 - 1)$ line of Figure 2 was the most reliable reflection of the efficiency of recombination. The fractions' recombination which occur with scrambling would then be distinct from the total recombination and are listed in the last column of Table V. This possibility is made more serious by our observation[7] of the possibility of the formation of *t*-butyl peracetate from the corresponding hyponitrite with some retention of the identity of the carbonyl oxygen atom. Against this possibility is the fact that the decarboxylation of the acetoxy radical is expected to be fast enough to compete with combination so that a nonzero intercept ($k_2 \sim k_c$) is expected when the acetoxy species is involved. The implication of a zero intercept is that the only kinetically important step in the forward direction is diffusive separation and therefore none of the isotope effect on the decarboxylation step can enter k_0. The values of k_0/k_0' for the present case (**6**) are predicted and observed to be too small to be of any value in establishing this expectation. However, in the earlier more accurate determinations with acetyl peroxide,[2] the values of k_0/k_0' were large enough to militate against such a possibility. However, the amount of reliable data presently available is too limited to rule it out completely.

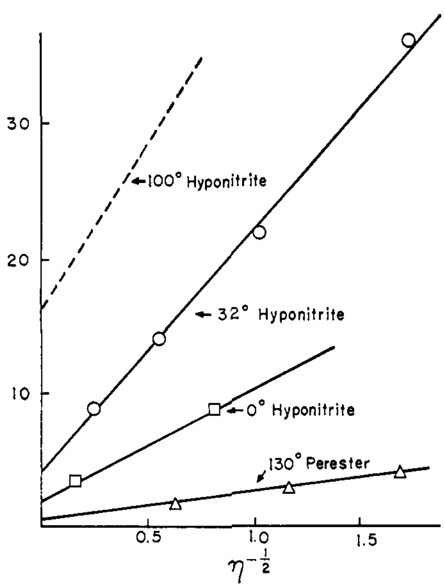

Figure 3. ⊙, $(1/y) - 1$, hyponitrite 32°; □, $(1/y) - 1$, hyponitrite 0°; ----, $(1/y) - 1$, hyponitrite 100° (extrapolated); △, k_0/k_s, peracetate 130°.

Square Root Fluidity Dependence. It should be remembered that there exists the alternative model proposed by Martin and coworkers[13,15] which can be used to fit all of the observed square root fluidity dependences. Here one assumes that k_c, the rate constant for combination, is the quantity which varies with fluidity giving rise to the observable changes in k_0, k_s, or yield. The quantitative connection is that pointed out in ref 2 with the following elaboration.

The combination rate constant may be assumed to be proportional to the reciprocal of the mean separation distance for the pair during its lifetime (eq 3)

$$\overline{k}_c = \frac{A}{R_0 + \delta R} = \frac{A}{R_0 + \sqrt{2D\delta}} \tag{3}$$

where R_0 is separation at time 0 and δR is the mean square displacement distance which is proportional to square root of fluidity.[7,11] The relationships of the

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[14] W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

[15] J. C. Martin and J. W. Taylor, *J. Amer. Chem. Soc.*, **89**, 6904 (1967).

functions of observable rate constants (k_0, k_s) follow simply and are given as eq 4

$$\frac{1}{(k_1/k_0 - 1)} = \frac{k_1}{k_s} - 1 = \frac{k_0}{k_s} = \frac{k_2}{k_c{}^\infty} + \frac{k_2}{k_{c'}} \qquad (4)$$

where $1/k_c{}^\infty = R_0/A$ defines the combination rate constant at infinite viscosity and $1/k_c' = (2D\tau)^{1/2}/A = BK_2[(\tau/\eta)^{1/2}]$ defines the viscosity sensitivity term. Substituting gives eq 5

$$\frac{1}{(k_1/k_s - 1)} = \frac{k_1}{k_s} - 1 = \frac{k_0}{k_s} = \frac{k_2}{k_c{}^\infty} + Bk_2\sqrt{\frac{\tau}{\eta}} \qquad (5)$$

Again a square root fluidity dependence is predicted. The intercepts in (5) have the identical meaning as those of our model. However, the physical meaning of the viscosity sensitivity term is somewhat different.

The sense of (5) is that a change in rate of combination results from a change in *rate constant* for the same concentration of pairs at all viscosities. The sense of our model is that changes in *rates* of combination occur due to changes in concentrations of pairs existing within the combination diameter. Our model[7,11] can be made to give (5) identically if the lifetime of the pair is set equal to $1/k_2$ rather than the reduced value given in ref 7. This alternative formalism does not therefore allow any new resolution of the discrepancy shown in Figure 2 and the problem of a constant *vs.* variable k_1 remains.

It should be emphasized that the linear behavior with the square root of fluidity may be a fortuitous result of the response of the diffusion coefficients of the radicals to viscosity. The equations derived by Noyes[16] to treat diffusion combination competitions could be applied if one merely assumes that D is proportional to some variable power of viscosity rather than a Stokes–Einstein dependence.[17] A plot of measured D for benzene[18] *vs.* square root fluidity is in agreement with this possibility. Measured diffusion coefficients for substances in media of widely varying viscosities are needed in order to answer this question.[17] However, the value of the plots corresponding to eq 2, such as shown in Figure 3, is not completely dependent on being connected to a formal model, such as the one which we have proposed.[7,11] The most important significance of the treatment is in allowing quantitative comparisons of combination–diffusion competitions which can be most safely considered as entirely empirical. The difference in the relative combination probability of the acetoxy-*t*-butoxy pairs from *t*-butyl peracetate and the corresponding hyponitrite (**9**), shown in Figure 3, *is independent of the detailed interpretation of the linear square root fluidity dependence.* Such a large difference is not apparent in the k_0/k_s observations made on benzoyloxy-*t*-butoxy pairs generated from the corresponding sources.[19]

The large reduction in recombination probability for the acetoxy-*t*-butoxy pair from **9**, compared to that from the perester, may be a result of partial concerted three-bond cleavage (O–N, N–O, C–C) of the hyponitrite rather than of the intervening nitrogen molecule. Tests for this possibility using kinetic and isotope effect studies in the hyponitrite series are presently under way. It is also possible that the acetoxy radical, generated in the deamination, undergoes decarboxylation more rapidly than that from the perester. Establishing this will be more difficult since it requires an understanding of the "normal" behavior which is complicated by the considerations above. With more comparisons of identical pairs generated from both single bond and deaminative routes, a distinction should be made possible.

Experimental Section

Proton nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer. Infrared measurements were made on a Beckman IR-7 instrument. Mass spectral determinations were made using a modified Consolidated Electrodynamics 26-614 residual gas analyzer. Microanalyses were by Berkeley Analytical Laboratories.

Materials. Chlorobenzene, *t*-butyl hydroperoxide, and isooctane were purified by the method described previously.[2] Nujol was used without purification. *p*-Nitrophenylacetic acid and *p*-methoxyphenylacetic acid were obtained from Aldrich. Deuterioacetic acid was obtained from Bio-Rad Laboratories. Oxygen-18-labeled acetyl chloride was obtained by hydrolysis of acetonitrile[7] and the action of oxalyl chloride on the labeled sodium acetate. The oxygen-18-labeled phenylacetic acids were obtained by hydrolysis of the corresponding acid chlorides. The deuterated phenylacetic acids were obtained by refluxing in excess deuterium oxide in the presence of base. Potassium hydroxide in high concentration was required for the methoxy compound and these conditions allow some oxygen exchange which accounts for the greater than natural abundance of oxygen-18 in the carbon dioxide from deuterated **8**. Potassium carbonate was used with the *p*-nitro acid and no oxygen-18 exchange appeared to have occurred because of the lower pH.

The peresters were prepared by the method of Bartlett.[3] The purification of **6** was by column chromatography over basic alumina. Its purity was judged by nmr and infrared spectra. Peresters **7** and **8** were prepared in a similar fashion. The final purification after column chromatography was by recrystallization. Deuterium contents of the deuterated compounds were greater than 96% as judged by quantitative nmr analyses.

Kinetics Methods. The infrared and double labeling kinetic methods have been described.[1,2]

Oxygen-18 Analysis of Partially Decomposed 6. The method of analyzing *t*-butyl peracetate samples recovered after partial decomposition was identical with that given in ref 7 except for the purification of the *p*-nitroperbenzoate. Pure samples of this material could be obtained by preparative thin layer chromatography over silica gel using hexane–ethyl acetate (1:1) as the liquid phase. One recrystallization of the material obtained in this way gave a sharp melting (79–79.5°) compound. The oxygen-18 content of the carbon dioxide obtained from this pure material was identical with that obtained from the unpurified crude product in every case. The major impurity was methyl *p*-nitrobenzoate; also isolated by thin layer chromatography.

Viscosity Determinations. Viscosities of hexane–oil mixtures were determined by comparison with *n*-butyl alcohol using Ostwald viscometer tubes of several sizes. The values at 130° were by extrapolation using the standard Arrhenius relationship. The measured values are listed in Table VI.

Table VI. Viscosity (Poise × 10^2)–Temperature Measurements

T, °C	Hexane	60% hexane[a]	30% hexane[a]	Oil
40.2	0.259	0.940	3.854	
47.1	0.247	0.885	3.486	37.42
60.2	0.218	0.744	2.564	20.97
75.1		0.629	1.929	12.09
84.8			1.653	8.86
97.5				6.56
130.1[b]	0.130	0.378	0.820	2.44

[a] Volume per cent hexane. The remainder made up as paraffin oil. [b] Extrapolated.

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[16] R. M. Noyes, *Progr. Reaction Kinetcs*, **1**, 131 (1961).

[17] This possibility is essentially equivalent to Pryor's treatment and is being tested further. Professor J. M. McBride has also communicated to us privately that his group is examining this question.

[18] D. J. Trevoy and H. G. Drickamer, *J. Chem. Phys.*, **17**, 1117 (1949).

[19] T. Koenig, M. Deinzer, and J. A. Hoobler, *J. Amer. Chem. Soc.*, in press.