

E. That equilibration in hexane was slow was proved by recrystallizing 5.8 g of enol from boiling hexane and recovering 5.2 g (90%) of material containing less than 5% keto. When 200 mg of either isomer was refluxed 5.5 hr in 25 ml of hexane, the keto gave a mixture containing 51% keto while the product from the enol contained 43% keto. After refluxing for 24 hr, the keto gave a keto:enol ratio of 43:57, showing that equilibration had not been complete after 5.5 hr. The enol gave a 45:55 ratio after 24 hr. The latter mixture also contained 4% of indole while the mixture from the keto isomer contained about 12% indole.

F. The keto isomer was heated without solvent for 3 hr on the steam bath. The product had a keto:enol ratio of 82:18. The enol tautomer gave a 70:30 ratio, and, in addition contained about 9% of oxindole and a trace of indole. When the keto compound was heated for 4 hr at 120–125°, the complex mixture appeared to contain 36% oxindole, 34% keto, 20% indole, and 10% enol. Similarly, the enol gave a mixture containing 46% oxindole, 27% indole, 19% keto, and 8% enol. It should be noted that the presence of oxindole is based solely on the sharp signal at δ 3.63, so this assignment must be considered tentative.

N-Benzoyl-N-(*o*-carboxymethyl)phenylanthranilic Acid. In our earlier paper,² we reported that hydrolysis of I with aqueous KOH gave a compound which we believed was a half-ester N-benzoyl acid. The carbonyl band at 5.78 μ was assigned to the ester group. However, the nmr spectrum (CD₃SOCD₃) clearly shows that no ester group is present. The product is actually the expected dibasic acid, one of the carboxyl groups absorbing at an unusually low wavelength.

Anal. Calcd for C₂₂H₁₇NO₅: C, 70.66; H, 4.60; N, 3.75; neut equiv, 197.0. Found: C, 70.39; H, 4.57; N, 3.73; neut equiv, 187.7.

Keto-Enol Mixture, XI and XII. The reaction was followed by tlc using unpurified CHCl₃ (stabilized with ethanol) to develop the

plates. The amide I gave a circular spot, R_f 0.15. The oxindole III gave an elongated spot, centered at R_f 0.10. The indole IV, as well as the keto-enol mixture had R_f 0.40, while the indole acid remained at the origin. The R_f values were not always reproducible. The mixtures were generally acidified with acetic acid before putting on the plate.

A. To 1.21 g (3 mmol) of amide I in 15 ml of dry benzene, was added at room temperature 151 mg (2.8 mmol) of "new" sodium methoxide. After stirring 2 min, tlc showed, in addition to starting I, a strong spot at R_f 0.40. After 7 min, the solid had dissolved, and the clear light brown solution was found to contain only a trace of I. A trace of oxindole was also present but the only predominant spot was that at 0.40. The tlc picture remained the same after 1 hr. The mixture was cooled in an ice bath and 0.3 ml (3.6 mmol) of concentrated aqueous HCl was added. After brief stirring, the organic material was extracted with ether, the extracts were dried, and the solvent was removed below room temperature to give a tan gum which, by nmr, contained about 30% keto XII and 13% enol XI. The gum was converted into indole IV (first part of Experimental Section, C, above).

Use of 0.2 ml (3.5 mmol) of acetic acid for the acidification in a parallel run gave a mixture which contained 40% keto XII (δ 3.83, 3.65, 5.78), 25% enol XI (δ 3.78, 3.65, 13.5), and about 10% indole IV (δ 3.72, 3.40). The NH peak was found at δ 9.28. Other constituents of the mixture were not identified, although starting amide I must have comprised roughly 7% of the mixture. Apparently little if any oxindole was present.

B. In another parallel run, after 70 min at room temperature, instead of adding acid, 108 mg (2 mmol) of additional sodium methoxide was added and stirring was continued. Within 2 hr, the spot with R_f 0.4 (XI plus XII) was gone, being replaced by the typical elongated oxindole spot. The usual work-up with excess HCl, afforded 0.57 g (51%) of oxindole III, mp 127–134°.

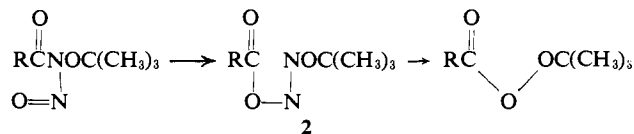
Thermal Decompositions of N-Nitrosohydroxylamines. II. N-Acetyl-N-nitroso-O-*t*-butylhydroxylamine

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Abstract: The decomposition of N-acetyl-N-nitroso-O-*t*-butylhydroxylamine has been studied under conditions of varying viscosity. The products include *t*-butyl peracetate and methyl *t*-butyl ether. The yields of these products increase with increasing viscosity. Oxygen-18-labeling studies show the perester is formed with at least 92% equilibration of the carbonyl oxygen label. The amount of cage combination from the deaminative radical pair is significantly lower than that which occurs from decomposition of the corresponding *t*-butyl peracetate.

Oxy-oxy radical combination reactions have been the subject of several recent investigations.¹ Our preliminary study² of the decomposition of N-benzoyl-N-nitroso-O-*t*-butylhydroxylamine (**1a**) suggested that this class of compounds could serve as a convenient source of acyloxy-*t*-butoxy radical pairs under conditions where the corresponding peresters are stable. We now



1a, R = C₆H₅
b, R = CH₃

(1) (a) H. Kiefer, and T. G. Traylor *J. Amer. Chem. Soc.*, **89**, 6667 (1967); (b) W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967); (c) J. C. Martin and J. Taylor, *ibid.*, **89**, 6904 (1967).

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

wish to report the results of our studies on the products of decomposition of N-acetyl-N-nitroso-O-*t*-butylhydroxylamine (**1b**) under conditions of varying viscosity.

Results

Solutions of the starting nitroso compound were obtained by nitrosation of N-acetyl-O-*t*-butylhydroxylamine with nitrosyl chloride and pyridine at low temperature. The infrared spectra of freshly prepared solutions obtained in this way show nitroso group absorption at 1541 cm⁻¹ and carbonyl absorption at 1762 cm⁻¹. The nmr spectra of such solutions show singlets at 1.22 and 2.75 ppm in a 3:1 intensity ratio. The visible spectra of such solutions show weak maxima at 391, 407, and 427 m μ . All of these observations are in accord with expectations for a simple N-nitroso compound.³

The rapid rearrangement of the first nitrosation product is evident from the infrared spectra by the disappearance of the 1541- and 1762-cm⁻¹ peaks and the simultaneous appearance of a new band at 1797 cm⁻¹. Figure 1 shows the rise and the decay of the 1797-cm⁻¹ band in paraffin oil and hexane. There is no indication of any change in the rates of formation or disappearance of the rearrangement product with changing viscosity though a 20–30% change would be difficult to rule out. The linear parts of the first-order decay curves give the same rate constant (0.25 min⁻¹) in both media.

The rearrangement is also detectable from the nmr spectra in which the two original singlets at 1.22 and 2.75 ppm decrease and two new singlets at 1.41 and 2.15 ppm (3:1 intensity ratio) appear. The visible spectrum shows the disappearance of the long-wavelength maxima. All of these spectral changes occur with a half-life of approximately 10 min at room temperature in carbon tetrachloride. Gas evolution at room temperature is less rapid than rearrangement.

These observations appear to be in accord with a simple rearrangement of the nitroso compound (1) to the azoacylate (2) which is apparently a metastable intermediate in this series of compounds.⁴ This supposition of the structure of the rearrangement product is made largely by analogy with the behavior of other nitroso amides⁵ and is not unambiguously demanded by these spectral observations.

The rearrangement product decomposes with the evolution of nitrogen on prolonged standing at room temperature or on warming. The products isolated from the over-all sequence are listed in Table I. All of these products can be ascribed to the intervention of acetoxy-*t*-butoxy radical-pair intermediates. The

Table I. Products^a of Decomposition of 1b at 32.4°

Product	moles/mole ^b
N ₂	1.00
CO ₂ ^c	0.93
CH ₄	0.57
(CH ₃) ₃ COH	0.67
CH ₃ OC(CH ₃) ₃	0.088
CH ₃ CO ₃ C(CH ₃) ₃	0.025

^a Carbon tetrachloride-hexane ($\eta = 0.33$ cP). ^b Based on starting nitroso compound 1b. ^c Methyl chloride was present but not determined.

Table II. Viscosity Variation in Yields^a at 32°

Vol % paraffin oil ^b	$\eta \times 10^2$, P	CH ₃ CO ₃ - C(CH ₃) ₃	CH ₃ OC- (CH ₃) ₃
0	0.331	0.027	0.089
33.3	0.934	0.045	0.163
58.4	3.37	0.067	0.325
83.4	16.99	0.102	0.417
83.4 ^c	36.00	0.25	

^a Moles per mole of nitroso compound. ^b Solvents contain 16.6% carbon tetrachloride, stated amount paraffin oil, and the remainder, hexane. ^c 0°.

(3) J. H. Cooley, P. T. Jacobs, M. A. Kahn, L. Heasley, and W. D. Goodman, *J. Org. Chem.*, **30**, 3062 (1965).

(4) The correctness of the structural assignment of the rearrangement product does not affect the main purpose of the present investigation which is the study of its decomposition products. Further structural data are being sought presently.

(5) R. Huisgen and G. Horeld, *Ann.*, **562**, 137 (1949); R. Huisgen and L. Krause, *ibid.*, **574**, 157 (1951); D. H. Hey, J. S. Webb, and G. H. Williams, *J. Chem. Soc.*, 4657 (1952).

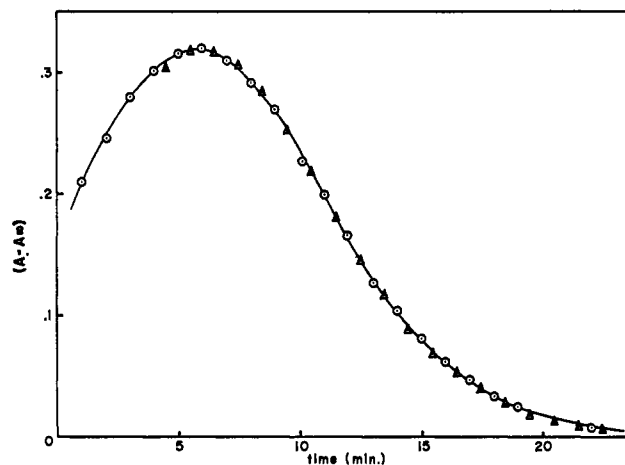
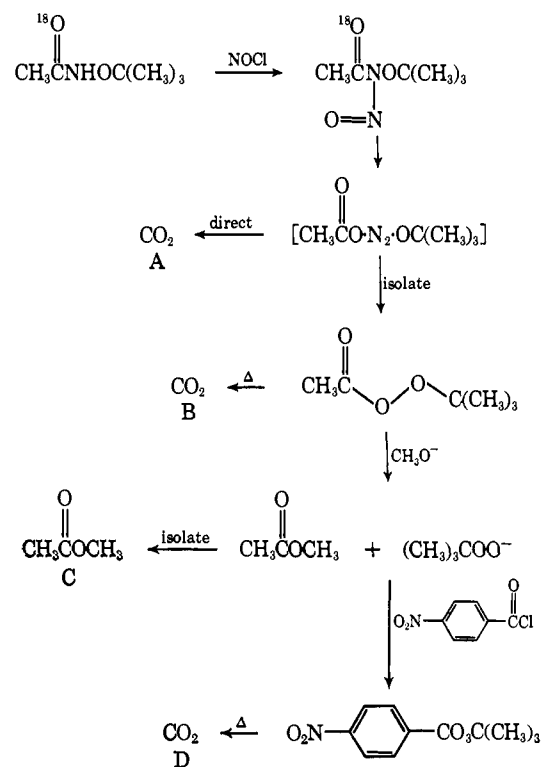


Figure 1. Optical density at 1797 cm⁻¹ vs. time at 42° in (○) paraffin oil, and (△) hexane, $k = 0.25$ min⁻¹.

methyl *t*-butyl ether and *t*-butyl peracetate yields increase with increasing viscosity. Data on these variations are summarized in Table II.

While the increasing yield of perester with increasing viscosity supports the notion that this product arises from geminate combination of the radical pair, four- or six-ring cyclic processes can also be invoked to explain its formation. Oxygen-18 experiments were therefore carried out to determine the extent to which such paths might be important. The analysis was carried out as outlined in Scheme I.

Scheme I



The carbon dioxide formed directly from the nitroso compound decomposition was collected and used to assay the amount of oxygen-18 in the carbonyl of the starting material. The perester product was isolated and treated with methoxide in methanol and the product methyl acetate isolated by glpc. The 61/59 mass spec-

Table III. Oxygen-18 Labeling Results (See Scheme I)

Compound	Total % excess ¹⁸ O	% equilibrated
CO ₂ ^a (direct) (A)	1.382, 1.381	
CO ₂ ^{a,b} (peracetate product) (B)	1.363	
CH ₃ CO ₂ CH ₃ ^c (C)	0.744, 0.745	92
CO ₂ ^a (<i>p</i> -nitro perbenzoate) (D)	0.660, 0.642	94
CO ₂ ^a (peracetate control) ^d (E)	1.297	
CH ₃ CO ₂ CH ₃ ^e (control) ^e (F)	1.283	
CO ₂ ^a (<i>p</i> -nitro perbenzoate from E) ^f (G)	0.000	

^a Using 46/44 mass spectral ratio, corrected for instrument and carbon-13. ^b This value may be low due to water exchange. See ref 16. ^c Using 61/59 mass spectral ratio corrected for instrument and carbon-13. ^d Carbon dioxide isolated from the decomposition of authentic *t*-butyl peracetate-carbonyl-¹⁸O. ^e Methyl acetate obtained from authentic *t*-butyl peracetate-carbonyl-¹⁸O, (the same as that used in E) after treatment with methoxide. ^f Carbon dioxide from decomposition of *p*-nitro-*t*-butyl perbenzoate which was isolated from the residue from G after treatment with *p*-nitrobenzoyl chloride.

Table IV. Oxygen-18 Equilibration in *t*-Butyl Peracetate

46/44 ^a direct	Temp, °C	Time, hr	Fraction perester recovd	46/44 ^a <i>p</i> -nitro perester	Fraction equilibrated	<i>k</i> ₀ / <i>k</i> _s ^e
0.01695	100 ^b	24	0.46	0.00653	0.38	1.6
0.01670	97 ^c	31	0.48	0.00695	0.45	1.2
0.01670	124 ^c	1.5	0.36	0.00657	0.39	2.0
0.01670				0.00409 ^d		

^a Corrected for instrument and carbon-13. ^b Paraffin oil, $\eta \sim 5$ cP. ^c Paraffin oil, 0.1 *M* styrene added. ^d Control sample of labeled perester subjected to methoxide-*p*-nitrobenzoyl chloride cycle without prior heating. ^e *k*₀ is the apparent rate constant for decomposition of perester as indicated by fraction recovered. *k*_s is the apparent rate constant for scrambling of oxygen-18 as measured by 46/44 mass ratios of carbon dioxide from *p*-nitro perester.

tral peak ratio was used to assay the oxygen-18 content of the ester.⁶ Control experiments were carried out to show that no equilibration of the oxygen atoms occurs during the treatment with methoxide.

The residue from the methoxide reaction was dissolved in water and *p*-nitrobenzoyl chloride added at 0°. The product *p*-nitrobenzoate perester was isolated and decomposed and the carbon dioxide produced used to assay its oxygen-18 content. These results are summarized in Table III.

The results of the oxygen-18 studies show that at least 92% of the label becomes equilibrated in the formation of the perester product. The oxygen-18 content in the carbonyl position of the perester product is high while that in the alkyl position is low. Both of these results suggest that some of the perester is formed with retention of the label in the carbonyl position. This could be an indication that the cage combination occurs in competition with the randomization of the label or that a four-ring cyclic process is responsible for a small amount of the perester product. Due to the difficulty of purifying the isolated peresters the uncertainty in our measurements could be as much as 8%. However, the fact that 92% of the label is equilibrated supports the radical-pair origin for the major portion of the reaction.

In order to make a comparison of these results with the same radical pair generated *without* the intervening nitrogen molecule, a sample of carbonyl-labeled perester was partially decomposed. The recovered ma-

(6) Deuterium-labeling studies in these laboratories have shown the 59 peak in the mass spectrum of methyl acetate is the O⁺≡COCH₃ ion formed by a simple fragmentation of the parent ion: unpublished work by R. Cruthoff.

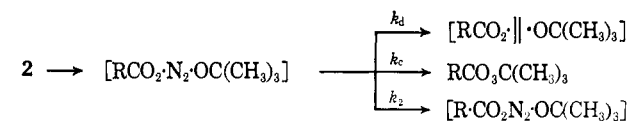
terial was subjected to the analytical scheme discussed above. These results are summarized in Table IV.⁷

Discussion

The qualitative observations of increasing yields of perester with increasing viscosity together with the isolation of radical products such as methane suggest a radical-pair mechanism for the formation of the perester. The oxygen-18 distribution of this product also largely supports this idea although the label could have been scrambled before the actual decomposition by reversible ion-pair formation. Scheme II summarizes our attempts to treat the yield data in a quantitative fashion assuming radical-pair intermediates.

In this scheme, *k*_c is the rate constant for geminate combination of the radical pair, *k*₂ is the rate constant for decarboxylation, and *k*_d is the rate constant for diffusive separation of the radical pair. We assume the

Scheme II



only fluidity ($1/\eta$) sensitive rate constant is *k*_d. Equation 1 gives the function of yield (*y*) which would be expected to vary in a simple way with fluidity.

$$\frac{1}{y} - 1 = \frac{k_d}{k_c} + \frac{k_2}{k_c} \quad (1)$$

In particular, when fluidity is reduced to zero, the intercept should give the ratio *k*₂/*k*_c. We expected that *k*_d would be a linear function of fluidity but our initial studies² with the benzoyl compound (1a) showed this was not the case. The present results with the peracetate and methyl *t*-butyl ether yields are similar. Reasonably good linear relationships are obtained when the left member of (1) is plotted *vs.* the square root of the fluidity (Figure 2). Our original expectation could thus be realized if, in fact, *k*_d were to vary as $(1/\eta)^{1/2}$ instead of $1/\eta$.

A justification of this square-root dependence is possible in the following way. The *time-dependent* rate constant for diffusive separation can be defined as the root-mean-square displacement distance (*r*) for the particle during a time (*t*) divided by the distance it must travel to have escaped multiplied by the time interval

(7) The listed *k*₀/*k*_s ratios are probably maximum values due to the complications of induced paths which contribute to *k*₀ but not to *k*_s. The effect of added styrene is in this direction.

(eq 2) where ρ is an effective collision diameter and R_0

$$k_d = r/(\rho - R_0)t \quad (2)$$

is the initial distance of separation. The root-mean-square distance of separation given by the theory of Brownian movement⁸ is

$$r = (2Dt)^{1/2} \quad (3)$$

where D is the effective diffusion coefficient for the pair which brings in the fluidity dependence ($D \propto 1/\eta$). The formal rate constant for diffusive separation then becomes

$$k_d = \sqrt{\frac{2D}{t}} \frac{1}{\rho - R_0} \quad (4)$$

Substitution into eq 1 gives

$$\frac{1}{y} - 1 = \sqrt{\frac{2D}{t}} \frac{1}{k_c(\rho - R_0)} + \frac{k_2}{k_c} \quad (5)$$

The time interval of interest is the reduced lifetime of the pair

$$\tau = \frac{\tau_2\tau_c}{\tau_2 + \tau_c} \quad (6)$$

where τ_2 and τ_c are the reciprocals of the corresponding rate constants. Substitution into (5) gives

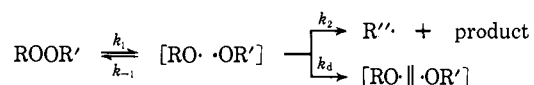
$$\frac{1}{y} - 1 = \frac{1}{\rho - R_0} \sqrt{2D\tau_c \left(1 + \frac{\tau_c}{\tau_2}\right)} + \frac{\tau_c}{\tau_2} \quad (7)$$

Equation 7 thus predicts the yield function should vary as the square root of the fluidity. It also predicts that the intercepts of all of the plots will be zero (for $\rho > R$) except when k_2 (which can be any competing process such as scavenging, hydrogen atom abstraction or β scission) is comparable to the combination rate constant, k_c . The intercepts (Figure 2) are zero for both the *t*-butyl perbenzoate formation, reported previously,² as well as the methyl *t*-butyl ether yields of the present work. However, the intercept for the *t*-butyl peracetate reaction is *ca.* 4. The decarboxylation of acetoxy radicals is thought to be a facile process and thus the positive intercept is a sensible result.

If we adopt the present model at its face value and assume k_2 for the acetoxy radical at 30° is 1×10^9 , then τ_c in this case is 4×10^{-9} sec. If we assume an effective diffusion coefficient of 1×10^{-5} cm²/sec for the acetoxy-*t*-butoxy radical pair at a viscosity of 1 cP, then the value of $\rho - R_0$ is 4 Å. Assuming R_0 is 6 Å, ρ is 10 Å. Thus the model is at least dimensionally reasonable.

The model can be easily applied to the measurement of either the rate of disappearance of a compound as a function of viscosity^{1b} or the ratio of disappearance to scrambling of oxygen-18 label^{1c} as a function of viscosity. Scheme III summarizes these cases. Here

Scheme III



k_d and k_2 have the same significance as above and k_{-1}

(8) W. Braun, L. Rajbenbach, and F. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

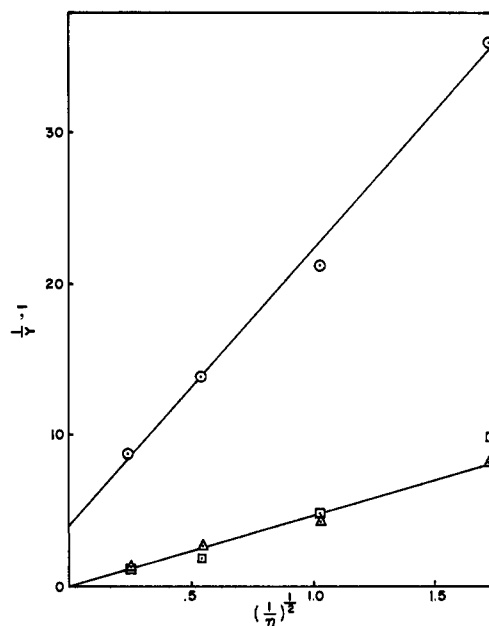


Figure 2. Viscosity variation for (○) *t*-butyl peracetate, (△) *t*-butyl perbenzoate, (□) *t*-butyl methyl ether (corrected by subtracting yield of *t*-butyl peracetate).

is analogous to k_c . Simple steady-state analysis shows

$$k_0 = \frac{k_1(k_2 + k_d)}{k_{-1} + k_2 + k_d}$$

and

$$k_s = \frac{k_1 k_{-1}}{k_{-1} + k_2 + k_d}$$

where k_0 refers to the observed rate of destruction of the peroxide and k_s refers to the observed rate of scrambling of the label.

Equations 8 and 9 give the functions of k_0 and k_s analogous to (1) which have the identical dependence on the fluidity.

$$\frac{1}{(k_1/k_0) - 1} = \frac{k_d}{k_{-1}} + \frac{k_2}{k_{-1}} \quad (8)$$

$$\frac{k_0}{k_s} = \frac{k_d}{k_{-1}} + \frac{k_2}{k_{-1}} \quad (9)$$

The yield of *t*-butyl peracetate from **1b** at a viscosity of 36 cP and 0° is 25%. From Figure 2, the corresponding yield at 32° is 16%. Extrapolation to 100° gives an estimate of *ca.* 5%. This can be compared to the observed value for k_0/k_s for *t*-butyl peracetate at approximately the same conditions of viscosity and temperature which is 1.5 (Table IV). This value of k_0/k_s corresponds to 40% return. The decomposition of **1b** thus gives radical pairs which have a very significantly reduced probability of recombining. In terms of eq 6, this can be seen to be a result of either a reduction in τ_c (increased rate of decarboxylation of the acetoxy radical formed from the deaminative reaction) or an increase in τ_2 (decrease in k_c for the deaminative radical pair). While a clear distinction is not yet possible, the order of the enhancement in the relative probability of diffusion is greater if we assume it to be due to an increase in τ_c . An increase in τ_c is also intuitively reasonable on the basis of the physical pres-

Table V. Results of Equation 1

Radical pair	Temp, °C	Source	Slope	Intercept	Ref
$\text{CH}_3\text{CO}_2\cdot \cdot \text{OC}(\text{CH}_3)_3$	32	1b	17	4.2	This work
$\text{CH}_3\cdot \cdot \text{OC}(\text{CH}_3)_3$	32	1b	4.5	0	This work
$\text{C}_6\text{H}_5\text{CO}_2\cdot \cdot \text{OC}(\text{CH}_3)_3$	32	1a	4.5	0	2
$2(\text{CH}_3)_3\text{CO}\cdot$	45	RON=NOR	4.0	0	1a
$2(\text{CH}_3)_3\text{CO}\cdot$	45	(ROOC(=O)-) ₂	5.1	0	1a
$\text{CH}_3\text{CO}_2\cdot \cdot \text{CH}_3$	60	(RCO ₂) ₂	1.0	2.3	8
$2\text{C}_4\text{H}_9\text{O}\cdot$	80	(RO) ₂	0.10	0	a
$2\text{CH}_3\text{CO}_2\cdot$	60	(RCO ₂) ₂	0.63	0.3	8

^a W. A. Pryor and K. Smith, unpublished work. We are grateful to Professor Pryor for making these results known to us before publication.

ence of the nitrogen molecule initially separating the two radicals.

Further support for this position is available from literature data. Table V summarizes the results of treatment of these data according to eq 6. All of the plots are reasonably linear in the high viscosity region (>0.5 cP) but show upward curvature in the more fluid solvents. Extrapolation of the linear parts of the curves gives zero intercepts for all of the examples cited except the decomposition of acetyl peroxide,^{1b,8} the methyl acetate production in the decomposition of acetyl peroxide⁸ and the present case of *t*-butyl peracetate formation from **1b**. All of these processes have a facile k_2 (decarboxylation) while none of the others do.

The slopes of the plots are related to the relative probability of diffusive separation. These slopes are large for radical pairs with intervening molecules and small for radical pairs with no intervening molecules. The large slopes are still observed for those cases where the intercepts are negligible. Thus, in terms of eq 7, the increased slope,⁹ when a molecule separates the pair, is probably due to an increase in τ_c since large slopes are observed even when τ_c/τ_2 is negligible.

The conclusion which we make from these studies is primarily that the presence of the nitrogen molecule strongly perturbs the probability for recombination. The possibility that an increased k_2 also contributes cannot be ruled out. This might be expected on the basis that the decomposition of **2** is more exothermic than that of the prester.

The problem of secondary recombination has been ignored. The present results indicate that if secondary recombination occurs, it must do so with a probability which is reduced by a factor which is more significant than a $1/r$ dependence. This follows since the mere presence of a nitrogen molecule reduces the probability by a significant factor. Direct comparisons of identical radical pairs formed with and without intervening molecules should provide a way of probing the factors governing their behavior at short separations in solution for which there is no adequate theory. It is our opinion that this model may not be indiscriminately applicable to comparisons of thermal and photo processes since the distribution of the excess photo excitation energy between translation and vibration could strongly influence the initial distance of separation of the radical pair as well as the behavior of both intervening and surrounding molecules. Studies of the photo-

chemical and thermal decompositions of ketenimes and azo compounds have already demonstrated such complications.¹⁰

Experimental Section

Proton nuclear magnetic resonance spectra were determined on a Varian A-60 spectrometer. Infrared measurements were made using a Beckman IR-7 instrument. Ultraviolet and visible spectral measurements were made on a Cary 15 recording spectrophotometer. Mass spectra were determined using a modified Consolidated Electrodynamic 26-614 residual gas analyzer. Gas-liquid partition chromatography was carried out on either an Aerograph Autoprep instrument or an Aerograph Hi-Fy Model 600-D instrument equipped with a Disk-Chart integrator Model 201-B.

Materials. Dioxane was purified by reflux over sodium for 2 days and distillation. *t*-Butyl alcohol was distilled from calcium oxide. Cumene was purified by shaking with concentrated sulfuric acid, separating, washing with water, and distillation. The first was discarded, and the remainder, bp 152°, was stored for short periods in a dark tightly stopped flask. Before using, it was checked for peroxides. *t*-Butyl hydroperoxide was purified by distillation.¹¹ Methanol, carbon tetrachloride, isooctane, *n*-hexane, acetonitrile, and toluene were all Spectroquality reagent grade from either Matheson Coleman and Bell, or Mallinckrodt Chemical Works. Paraffin oil, from Allied Chemical, was used without further purification.

***t*-Butylhydroxylamine Hydrochloride.** Initial studies were carried out with material prepared according to the method of Theilacker and Ebke.¹² A more convenient procedure is the basic hydrolysis of ethyl *N-t*-butoxycarbamate. An ethereal solution of ethyl azidoformate prepared from 0.54 mol of sodium azide and 0.45 mol of ethyl chloroformate¹³ was added to 470 ml of refluxing *t*-butyl alcohol. After refluxing for 7 days the evolution of nitrogen ceased, and the excess *t*-butyl alcohol was removed. The carbamate (43 g) was added dropwise to 400 ml of 5 *M* sodium hydroxide solution at 80°. The mixture was stirred vigorously for 3.5 hr. The cooled reaction mixture was extracted with three 200-ml portions of ether, and the combined extracts were dried over anhydrous sodium sulfate. The ethereal solution was cooled to 0.5° and dry hydrogen chloride gas was passed into the solutions. The hydrochloride was filtered off and washed with anhydrous ether, yield: 15.6 g (28% based on ethyl chloroformate).

***N*-Acetyl-*O-t*-butylhydroxylamine.** A solution of 10.5 g (0.083 mol) of *t*-butylhydroxylamine hydrochloride and 11.4 g (0.166 mol) of imidazole in 100 ml of acetonitrile was cooled to 0°. To the stirred solution was added dropwise 8.05 g (0.103 mol) of redistilled acetyl chloride. After complete addition (20 min) the reaction mixture was stirred for an additional 5 hr. The acetonitrile was removed. The entire residue was chromatographed over neutral Woelm alumina, activity IV, eluting with methylene chloride. After removal of the solvent, 10.4 g (95.0%) of white crystalline product was recrystallized from a solution of 180 ml of Skellysolve B and methylene chloride, 5:1, to give white needle-like crystals, mp 83°. The nmr spectrum in deuteriochloroform revealed *t*-butyl protons (singlet at δ 1.28) methyl protons (singlet at δ 2.01), and NH protons (singlet at δ 8.57) in the expected ratio.

(9) The relative slopes also contain the variations due to size and molecular weight differences (D) as well as the variations due to the changes in activation energies for the combination process, *i.e.*, τ_c may depend on other structural features of the pair in addition to the presence or absence of an intervening molecule.

(10) J. Fox and G. Hammond, *J. Amer. Chem. Soc.*, **86**, 4031 (1964).

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Anal. Calcd for $C_8H_{13}NO_2$: C, 54.95; H, 9.91; N, 10.69. Found: C, 54.86; H, 9.89; N, 10.51.

Infrared showed $\nu_{\max}^{Cl^{14}}$ 1672 (s) (amide $>C=O$) and 3240 cm^{-1} (weak) (NH).

N-Acetyl-N-nitroso-O-*t*-butylhydroxylamine. In a typical run, 523.6 mg (4.00 mmol) of N-acetyl-O-*t*-butylhydroxylamine, and 0.48 ml of dry pyridine were dissolved in 6 ml of carbon tetrachloride. The reactants were allowed to cool to -10° , and then a saturated solution of nitrosyl chloride in 12 ml of carbon tetrachloride was added dropwise under constant stirring. After complete addition of the nitrosyl chloride solution (20 min) stirring at -10° was continued for 1 hr. The reaction mixture was then washed successively at 0° with 25-ml portions of water, 10% hydrochloric acid solution, 10% sodium bicarbonate solution, and water. The organic layer was dried over anhydrous magnesium sulfate or potassium carbonate. After filtration the concentration of the nitrosated compound was estimated by nmr using dioxane as an internal standard. The nitrosated compound was never isolated and always kept as cold as possible while handling because of its extreme instability. All experiments were carried out using aliquots of these solutions.

Product Studies. The solution of nitrosated amide was added to breakseal flasks together with the solvent, hexane, and paraffin, to effect the proper viscosity of the reaction medium. The flasks were evacuated and after several freeze-thaw cycles were sealed off at reduced pressure. Decompositions of the reactants were carried out in constant temperature baths. Yields of gaseous products were determined utilizing a calibrated vacuum line and mass spectrometry. Peresters were distilled quantitatively from the reaction mixture under high vacuum and determined using the carbonyl absorption $\nu_{\max}^{Cl^{14}}$ 1780 cm^{-1} in the infrared. All other liquids were determined by glpc. For *t*-butyl methyl ether a $\frac{1}{8}$ in. \times 20 ft column packed with 30% TCEP on 60-80 Firebrick was used. *t*-Butyl alcohol was determined on a $\frac{1}{8}$ in. \times 14 ft column packed with 10% Carbowax 20M on 60-80 Firebrick. Calibration curves were made by plotting injected volumes of solution of known concentration vs. area.

Acetyl Chloride- ^{18}O . To 40 g of water enriched with 1.58 atom % excess oxygen-18 was added with cooling 22 g (0.406 mol) of sodium methoxide. After all reaction had subsided, 16.7 g (0.406 mol) of acetonitrile was added. The reaction mixture was refluxed for 4 days under a stream of nitrogen. When no more ammonia was detectable, the excess water and solvent were removed. The sodium acetate was fused under reduced pressure. A quantitative yield of 31 g was obtained. The sodium acetate (24 g, 0.294 mol) was added in small portions to an ice-cold solution of 37.5 g (0.295 mol) of oxalyl chloride¹⁴ and 150 ml of toluene in a flask fitted with a stirrer and an efficient reflux condenser. Each addition of sodium acetate resulted in a vigorous evolution of gas, which was allowed to subside before a subsequent portion was added. After complete addition the reaction mixture was heated to $60-70^\circ$ for 3 hr. After cooling and filtration, the acetyl chloride was distilled, bp $50-55^\circ$, from the reaction mixture. Some toluene was also distilled and the amount was estimated by nmr. No attempt was made to purify the acetyl chloride further. The adjusted yield was 17 g (74%).

N-Acetyl-O-*t*-butylhydroxylamine- ^{18}O . The procedure already described for the unlabeled compound was used except that acetyl chloride- ^{18}O was employed.

Anal. Calcd for $C_8H_{13}NO_2$: C, 54.95; H, 9.91; N, 10.69. Found: C, 54.87; H, 9.96; N, 10.47.

***t*-Butyl Peracetate- ^{18}O .** To an ice-cold solution of 48.6 g (0.540 mol) of *t*-butyl hydroperoxide and 19.6 g (0.218 mol) of pyridine was added 14 g (0.18 mol) of acetyl chloride- ^{18}O according to the method of Bartlett and Hiatt.¹⁵ After several attempts at purification by treatment with 25% potassium hydroxide solutions and chromatography over basic Woelm alumina, a singlet in the nmr, at slightly higher field than the *t*-butyl protons of the perester, still remained. This is believed to have been due to some di-*t*-butyl peroxyoxalate which resulted from any oxalyl chloride that was not

removed in the distillation of acetyl chloride- ^{18}O . This impurity, however, was effectively removed by allowing the perester to stand at room temperature for a week and then chromatographing over basic alumina. Nmr analysis in carbon tetrachloride showed *t*-butyl protons (singlet δ 1.30) and methyl protons (singlet δ 2.02) in the ratio, 3:1. Infrared showed $\nu_{\max}^{Cl^{14}}$ 1780 cm^{-1} (s) (perester $>C=O$).

Oxygen-18 Studies. A fivefold increase in reagent was used in the procedure already described for the preparation of a solution of N-acetyl-N-nitroso-O-*t*-butylhydroxylamine. The solution (100 ml), which was ca. 0.2 M in N-nitroso compound, was added to a 1-l. breakseal flask together with 347 g of paraffin oil. The flask was sealed off as described previously. After complete decomposition of the nitrosated compound at 32° , the 46/44 mass ratio for carbon dioxide was determined (A, Table III). The *t*-butyl peracetate was isolated and its yield determined (340-370 mg) by infrared in carbon tetrachloride. An aliquot of the carbon tetrachloride solution was dried over calcium chloride,¹⁶ the solvent removed, and the residue heated in isooctane. The carbon dioxide from this reaction was collected from a vacuum line and the oxygen-18 content determined (B, Table III). By adding small amounts of isooctane to the carbon dioxide, it was shown that the 46/44 mass ratio for carbon dioxide was not affected. An equivalent of sodium methoxide in 10 ml of methanol was added to the remainder of the perester, and the reaction mixture was stirred overnight at room temperature. The products were evaporated on a vacuum line giving methyl acetate and methanol as distillate and a solid residue containing sodium *t*-butyl peroxide.

The methyl acetate was collected by preparative glpc using a 0.25 in. \times 5 ft column packed with 10% Carbowax 20M on 60-80 Firebrick, and the 61/59 mass ratio was determined (C, Table III).

The residue was dissolved in ca. 20 ml of water and cooled to 0° . To this was added, under stirring, 415 mg of *p*-nitrobenzoyl chloride in 25 ml of methylene chloride. Vigorous stirring was continued for 5 hr. The organic layer was separated, washed three times with 25-ml portions of 10% sodium carbonate and then several times with 25-ml portions of water. The organic solution was dried over anhydrous calcium chloride and after filtration, the solvent was removed. The crystalline *p*-nitro-*t*-butyl perbenzoate was purified by passing a solution of it in methylene chloride over neutral Woelm alumina (activity IV). Infrared showed $\nu_{\max}^{Cl^{14}}$ 1765 cm^{-1} (s) (perester $>C=O$); mp $69-71^\circ$ (lit.¹⁷ 79°).

A solution of 20.5 mg (0.86 mmol) of this *p*-nitrobenzoyl perester and 4 ml of cumene in an evacuated breakseal flask was immersed in a bath at 145° for 3 hr. The carbon dioxide was collected from a vacuum line into a tube specially designed for mass spectral analysis. The 46/44 mass ratio was determined (D, Table III). In order to remove traces of cumene and other foreign matter, the remainder of the gas was purified by preparative gas chromatography using a 20-ft column packed with dibutyl phthalate. The 46/44 mass ratio for the carbon dioxide was determined again, and found to be the same as that for the unpurified sample.

A similar procedure was used for determination of oxygen-18 equilibration in *t*-butyl peracetate-carbonyl- ^{18}O (Table IV). A control sample of the labeled perester was carried through the sequence without partial decomposition. The *p*-nitroperbenzoate from this sample gave carbon dioxide with no excess oxygen-18 (G, Table III). All mass ratios were corrected for carbon-13 and instrumental variations.

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(16) The drying step was found to be essential since without it the carbon dioxide formed from heating the residue, obtained simply by evaporation of the solvent, contained irreproducibly low amounts of oxygen-18. This is probably due to water condensation into the sample during the extended periods of evacuation needed to pump the perester out of the oil solvent.

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