of starting material except for the presence of weak carbonyl absorption at 1700 cm.$^{-1}$.

Attempted Photooxygenation of Esters. The following ring-A and ring-B esters were photooxygenated in the usual way in pyridine with hematoporphyrin for periods that ranged from 72 to 144 hr.: **1b, 1c, 4b, 8d, 8e, 9b, 9c,** and **9e.** In each case work-up gave material whose infrared spectrum was the same as that of the starting ester. Other dyes (methylene blue, eosin-Y, erythrosin-B) were tried with esters **1b** and **1c** with the same results.

Effect of Sensitizer on Product Ratio from Cholest-4-en-3β-ol (**1a**). The alcohol (0.05 g./40 ml. of pyridine) was photooxygenated for 80 hr. under a standardized set of conditions with various sensitizers.

Initially 0.007 g. of the dye was used but more was added as needed during the reaction to compensate for bleaching. After normal work-up the enone content was determined directly from the absorption at 241 mμ. A portion of the product was oxidized with manganese dioxide to assay for remaining alcohol **1a**, and the epoxy ketone content was calculated by difference. In some cases the percentage of epoxy ketone was checked by the quantitative infrared technique. The correlation with the ultraviolet method was excellent when the enone proportion was small. An Aminco-Bowman spectrophotofluorometer (American Instrument Co.) was used to measure the fluorescence emission maxima of the dyes. Table I in the text summarizes the results.

Organic Peroxides. IV. Kinetics and Products of Decompositions of Cyclohexaneformyl and Isobutyryl Peroxides. BDPA as a Free-Radical Scavenger[1]

Robert C. Lamb,[2] Jas. Grady Pacifici, and Paul Wayne Ayers

Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia. Received March 17, 1965

The kinetics and free-radical efficiencies of the thermal decompositions of cyclohexaneformyl peroxide (*I*) and isobutyryl peroxide (*II*) in carbon tetrachloride were determined with excess α,γ-bis(diphenylene)-β-phenylallyl (*BDPA*) at temperatures between 30 and 85° in experiments in which initial BDPA concentrations were near 5 × 10^{-5} M. First-order rate constants obtained by this method differ by less than 10% from rate constants obtained by infrared and iodometric analysis in runs conducted at peroxide concentrations near 0.1 M. The rate constants and efficiencies obtained by the excess BDPA method are independent of the ratio of initial concentrations of BDPA to peroxide (Z$_0$/P$_0$). Product studies were performed (by g.l.c. and infrared analysis) on mixtures obtained from the decompositions of I and II in carbon tetrachloride, and in the same solvent containing excess BDPA. Evidence is presented which indicates that inversion compounds (RCOOCOOR)[3] are formed in the decompositions of both peroxides. While BDPA does not change the kinetics of decomposition of either peroxide significantly, the yields of some of the volatile products are changed drastically in its presence. Thus, alkyl chloride yields are reduced significantly in the presence of BDPA while the yields of carboxylic acid are increased substantially. The interpretation given to the latter effect is that acyloxy radicals are transformed into carboxylic acids by an unknown process by BDPA. Rate constants for decompositions of II in several other polar and nonpolar solvents at 40° were determined by iodometric assay. The solvent effects on the decomposition rate are similar to those reported recently by Pincock for the second-order reaction between pyridine and t-butyl peroxyformate.[4] Thus in nonpolar solvents, the rates increase with increasing solvent polarizabilities, while in polar solvents, the rates increase with increasing dielectric constants. In some of the nonpolar solvents in which the intermediate inversion compound is relatively stable, the yield of inversion compound increases significantly with increasing rate. These results suggest that the homolysis and the rearrangement of peroxide to inversion compound are two distinct modes of decomposition. Kinetics of decomposition of II in isooctane were also measured at various pressures between one and 3000 kg./cm.^{2}. The negative activation volume thus determined is another indication that the peroxide undergoes rearrangement.

Introduction

In a recent paper, two of us presented experimental evidence which showed that stable radicals (galvinoxyl, BDPA, and DPPH) could be used to determine simultaneously the rates and efficiencies in the decompositions of cyclohexanecarbonyl peroxide in benzene.[5] The present paper is an extension of that work, namely, a report of similar experiments performed upon cyclohexaneformyl peroxide (I) and isobutyryl peroxide (II) in carbon tetrachloride.
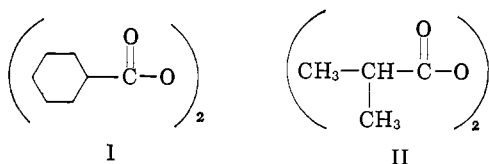
(3) F. D. Greene, H. P. Stein, C. Chu, and F. M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964).
(4) R. E. Pincock, *ibid.*, **86**, 1820 (1964).
(5) Paper III in this series: R. C. Lamb and J. G. Pacifici, *ibid.*, **86**, 914 (1964).

I   II

Galvinoxyl[6] was used extensively in the previous work.[5] Unfortunately, however, it was found that galvinoxyl undergoes considerable fading in pure carbon tetrachloride, even at rather low temperatures. Of the stable radicals at our disposal, only BDPA[7] behaved in a completely ideal fashion in carbon tetrachloride,[8] and for that reason it was used in this work.

Both of the peroxides used in this work have been studied previously. In 1959, in a survey of several related peroxides, Hart and Wyman reported a brief study of the decomposition of cyclohexaneformyl peroxide in carbon tetrachloride.[9] A study of the products of decomposition of isobutyryl peroxide in carbon tetrachloride has been made by Kharasch, Kane, and Brown.[10] In addition, a rather extensive study of the kinetics and products of the decomposition of II in isooctane has been reported by Smid and Szwarc.[11]

Results and Discussion

The results of kinetics–efficiency experiments which were determined from decompositions of peroxides I and II at low initial concentrations of BDPA (Z_0) and peroxide (P_0) are given in Table I. In these experiments the BDPA was present in excess in the sense that some remained after all the peroxide had decomposed. The rates were measured by following the rate of disappearance of the 490-mμ BDPA absorption, and efficiencies were obtained from the total amount of fading of this band from zero to "infinity" times.[5,12] In addition, the results of some iodometric and infrared kinetics runs on the two peroxides are reported in Table II. In all the experiments reported in Tables I and II the rates were followed through at least 2 half-lives. In most experiments, the rates were followed through more than 85% reaction.

(6) (a) G. M. Coppinger, *J. Am. Chem. Soc.*, 79, 501 (1957); (b) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, 22, 1435 (1957); (c) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, 84, 2596 (1962); (d) F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, 83, 3461 (1961); (e) F. D. Greene and W. Adam, *J. Org. Chem.*, 28, 3550 (1963).

(7) (a) C. F. Koelsch, *J. Am. Chem. Soc.*, 79, 4439 (1957); 54, 4744 (1932); (b) S. L. Solar and R. M. Lindquist, *ibid.*, 82, 4285 (1960); (c) S. L. Solar, *J. Org. Chem.*, 28, 2911 (1963); (d) R. Kuhn and F. A. Neugebauer, *Monatsh.*, 95, 3 (1964).

(8) Even carbon tetrachloride solutions of BDPA, when heated at 80° for 1 day or so, underwent a small change in absorbance. The absorbance at 490 mμ decreased very slowly at first, then *increased* slowly. Apparently, a very slow reaction occurs under these conditions which is not detectable at lower temperatures. In view of this, one may wonder why we report efficiencies at 85° in Table I. The explanation is that, at that temperature, the half-life of peroxide I is only 1 min. or so, and "infinity time" was taken as 20 min. In this short period, no change occurred in the absorbance of the control sample. The reader probably realizes that this explanation is not entirely free of objection, for if, as we say, the peroxide has a half-life of less than 2 min. at 85°, then a significant portion of it has decomposed before the sample vial has achieved bath temperature. Inasmuch as the efficiencies are slightly temperature dependent, it is probable that those reported for 70 and 85° are slightly low.

(9) H. Hart and D. Wyman, *J. Am. Chem. Soc.*, 81, 4891 (1959).

(10) M. S. Kharasch, S. S. Kane, and H. C. Brown, *ibid.*, 63, 526 (1941).

(11) J. Smid and M. Szwarc, *J. Chem. Phys.*, 29, 432 (1958).

(12) (a) R. C. Lamb, F. F. Rogers, Jr., G. C. Dean, Jr., and F. W. Voight, Jr., *J. Am. Chem. Soc.*, 84, 2635 (1962); (b) T. Koenig and W. Brewer, *ibid.*, 86, 2728 (1964).

Table I. Kinetics and Free-Radical Efficiencies of Cyclohexaneformyl Peroxide (I) and Isobutyryl Peroxide (II) in Carbon Tetrachloride Containing BDPA[a,b]

Run no.	$10^5 Z_0$	Z_0/P_0	$10^5(k_{obsd} \pm$ std. dev.), sec.$^{-1}$	$t_{1/2}$, min.	f	Temp., °C.
			Peroxide I			
1A	4.28	0.68	Too fast to measure		0.300	85
1B	4.28	1.33	Too fast to measure		0.300	85
2A	4.14	0.65	Too fast to measure		0.287	70
2B	4.14	2.18	Too fast to measure		0.288	70
2C	4.14	1.31	Too fast to measure		0.288	70
3A	4.28	0.85	130.2 ± 0.8	8.87	0.279	60
3B	4.28	0.68	132.1 ± 0.6	8.74	0.262	60
3C	4.28	1.33	128.1 ± 1.0	9.01	0.264	60
4A	4.28	0.68	43.9 ± 0.3	26.3	0.256	50
4B	4.28	1.33	44.7 ± 0.2	25.9	0.255	50
4C	4.28	1.33	44.8 ± 0.7	25.9	0.261	50
5A	4.14	1.31	20.8 ± 0.3	55.5	0.236	45
5B	4.14	0.65	21.4 ± 0.3	53.9	0.237	45
6A	4.28	0.85	6.72 ± 0.07	171.8	0.208	35
6B	4.28	0.68	6.60 ± 0.07	175.2	0.203	35
6C	4.28	1.33	6.61 ± 0.05	174.4	0.204	35
			Peroxide II			
7A	4.64	1.63	Too fast to measure		0.547	70
7B	4.64	2.45	Too fast to measure		0.549	70
7C	4.64	4.89	Too fast to measure		0.548	70
8	4.64	1.63	76.7 ± 0.5	15.0	0.528	60
9A	4.54	1.49	56.0 ± 0.1	20.6	0.519	55
9B	4.54	1.16	56.3 ± 0.1	20.5	0.519	55
10A	4.54	1.49	30.7 ± 0.1	37.7	0.505	50
10B	4.54	1.16	30.2 ± 0.1	38.4	0.500	50
11A	3.54	1.22	16.8 ± 0.1	68.7	0.498	45
11B	3.54	1.04	15.4 ± 0.1	75.0	0.492	45
11C	3.54	1.44	15.2 ± 0.2	75.7	0.491	45

[a] Excess BDPA was used in all experiments, in the sense that some BDPA remained after all the peroxide had decomposed. The rates were measured by following the decrease in absorbance of BDPA at 490 mμ. [b] Abbreviations used: Z_0 = (BDPA)$_0$; P_0 = initial molar concentration of peroxide. The free-radical efficiency, f, is so defined that $2f$ = yield of free radicals in mole/mole of peroxide.

Table II. Iodometric and Infrared Kinetics Runs of Peroxides I and II in Carbon Tetrachloride

Run no.	$Z_0{}^a$	$P_0{}^a$	$10^5(k_{obsd} \pm$ std. dev.), sec.$^{-1}$	$t_{1/2}$, min.	Temp., °C.
			Peroxide I		
12[b]	0	0.04	19.6 ± 0.3	59.0	45
13[c]	0	0.11	20.3	57.0	45
14[c]	0.10	0.11	20.3	56.8	45
			Peroxide II		
15[b]	0	0.10	56.0 ± 0.2	20.6	55
16[b]	0	0.10	28.5 ± 0.2	40.7	50
17[b]	0	0.10	15.35 ± 0.02	75.3	45
18[b]	0	0.08	7.85 ± 0.02	147.4	40
19[b]	0	0.08	1.78 ± 0.02	645.2	29.3
20[c]	0	0.05	29.5	39.0	50
21[c]	0.08	0.05	28.7	40.4	50

[a] Z_0 and P_0 are the initial molar concentrations of BDPA and peroxide, respectively. [b] Determined by iodometric titration. [c] Determined by infrared analysis, using the 1766- and 1770-cm.$^{-1}$ bands, respectively, for peroxides I and II.

The following points may be made about the data in Tables I and II.

(a) The results in Table I show that the rates and efficiencies in decompositions of both peroxides are
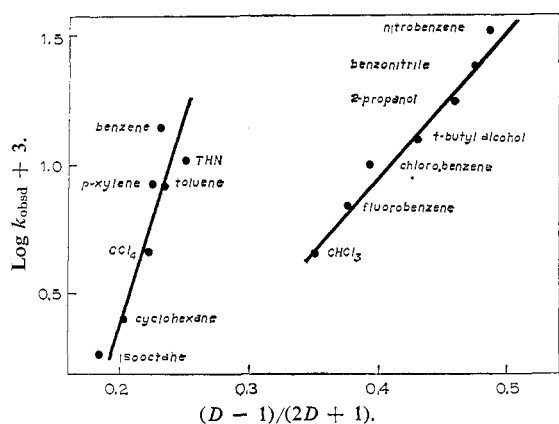
Figure 1. Plot of log (k_{obsd} + 3) vs. (D − 1)/($2D$ + 1) for decompositions of isobutyryl peroxide (Table III).

Table III. Kinetics of the Decompositions (at 40°) of Peroxide II in Various Solvents[a]

Solvent	P_0, M	Relative yields[b]	$10^5 k_{obsd}$, sec.$^{-1}$
Nitrobenzene	0.064		58.0
Benzonitrile	0.066		42.0
Isopropyl alcohol	0.061		30.5
t-Butyl alcohol	0.048		25.1
Benzene	0.062	4.0	24.0
Benzene	0.100	3.8	23.6
Tetrahydronaphthalene	0.097		17.5
Chlorobenzene	0.064		17.3
Toluene	0.050	3.2	14.3
Toluene	0.090	3.2	14.2
p-Xylene	0.128	3.3	14.0
Fluorobenzene	0.065		12.3
Carbon tetrachloride	0.097	2.3	7.8
Chloroform	0.048		7.5
Cyclohexane	0.138	1.3	4.5
Isooctane	0.100	1	3.2
Isooctane			3.0[c]

[a] All rates determined by iodometric titration. [b] Of inversion product. Absolute yields not possible because a pure sample of the inversion compound could not be obtained for comparison. Yield of inversion compound in isooctane was approximately 0.1 mole/ mole of peroxide decomposed. [c] Taken from ref. 11.

reproducible and are independent of the ratio of initial concentrations of BDPA to peroxide, Z_0/P_0. This helps establish that the decompositions are zero order in BDPA.

(b) The rates determined by measuring the fading of BDPA for solutions in which Z_0 and P_0 are near 5×10^{-5} M (Table I) are within 10% of those determined by iodometric titration and by infrared analysis at peroxide concentrations near 0.1 M (Table II).

(c) The decomposition rates of I and II determined by infrared analysis are the same for runs in pure carbon tetrachloride as in runs in which the stock solutions contained excess BDPA (runs 13, 14, 20, and 21 in Table II).

(d) Temperature coefficients of the rates may be summarized as follows. For peroxide I, $\Delta H^* = 23.8 \pm 0.4$ kcal.; $\Delta S^* = -0.56 \pm 0.25$ e.u. For peroxide II, $\Delta H^* = 26.0 \pm 0.3$ kcal.; $\Delta S^* = -5.5 \pm 0.5$ e.u.[13]

The kinetics experiments in Tables I and II clearly show that the decomposition rates of peroxides I and II are first order in peroxide and zero order in BDPA.

The results of a number of iodometric kinetics runs performed on the decompositions of peroxide II in a variety of solvents are given in Table III. The rate constants are approximate, for the runs consisted of only three or four points taken in the first 50-80% reaction. Although the data gave good first-order plots in all the runs, no attempt was made to estimate the errors in rate constants because of the small number of readings in each run. Nevertheless, two separate runs in benzene gave similar rate constants, and in addition the rate constant obtained in isooctane is near the value reported by Smid and Szwarc.[11]

In general, the rates increase with increasing dielectric constant of the solvent. However, a plot of log k_{obsd} vs. (D − 1)/($2D$ + 1)[14] (Figure 1) shows a distinct difference between the effects of polar and nonpolar solvents. The log k_{obsd} values for nonpolar

(13) All of the pertinent rate data in Tables I and II were used in calculating the activation parameters for peroxide I. In the calculation of the activation parameters for peroxide II, all pertinent rate data from Tables I and II were used except run 11A in Table I, which rate is substantially different from the other rates determined at 45° for peroxide II.

(14) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 140.

solvents give a fair correlation with the polarizabilities (per unit volume) of those solvents.

The general behavior of these data is very similar to those reported recently by Pincock for the second-order reaction between pyridine and t-butyl peroxyformate,[4] a reaction which amounts to a catalysis by pyridine of the decomposition of the perester to carbon dioxide and t-butyl alcohol. Pincock argued that this reaction proceeds through a concerted mechanism in which the proton is removed and the alkoxide ion and carbon dioxide are formed simultaneously, and suggested that the following limiting structure contributes to the resonance structure of the transition state.
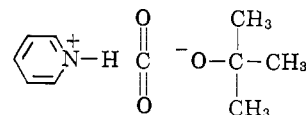
Unfortunately, while the data in Table III were being obtained it was not realized how similar in behavior the reactions are which are being compared here. However, by coincidence eight common solvents were used. Figure 2 is a plot of log k_{obsd} (isobutyryl peroxide) vs. log k_2 (pyridine-t-butyl peroxyformate) for those eight solvents. Except for the reactions in chloroform, the correlation is quite good. The slope of the plot is 0.5. The obvious conclusion is that a limiting polar structure similar to that above contributes to the structure of the transition state in the decomposition of isobutyryl peroxide, but that the
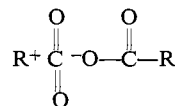
transition state in the decomposition of isobutyryl peroxide is not as polar (slope = 0.5) as is that of the destruction of t-butyl peroxyformate by pyridine.
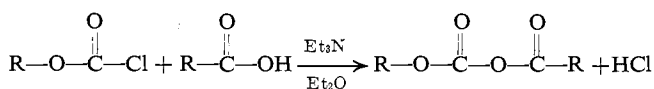
The behavior of the kinetics data in Table III is better understood, however, if it is first explained that in the decompositions of both peroxides "inversion"

compounds of the type RCOOCOOR are apparently formed as intermediates which subsequently decompose to give, predominantly, ester. This is not an unexpected development, in view of the recent communication by Greene, Stein, Chu, and Vane concerning decompositions of structurally related peroxides.[3,15]

The evidence upon which this assertion is based is as follows.

(a) In the decompositions of either peroxide, new infrared absorption bands appear in the carbonyl stretching region which are not due to peroxide, acid, or ester. Thus, infrared spectra of solutions of peroxide I in carbon tetrachloride show a peroxide carbonyl doublet initially at 1787 (w) and 1767 (s) cm.$^{-1}$. When heated, new bands appear in the infrared spectra at 1790 (s) and 1745 (w) cm.$^{-1}$, which persist long after all of the peroxide has disappeared. Similarly, carbonyl absorption bands due to peroxide II at 1798 and 1770 cm.$^{-1}$ are replaced by bands at 1760 and 1805 cm.$^{-1}$ upon heating solutions of peroxide II in carbon tetrachloride for a time period sufficient to destroy the peroxide.

(b) Although we have been unable to obtain samples of inversion compounds in sufficiently pure state to give correct combustion data, treatment of either carboxylic acid with the corresponding chloroformate[16] yields a liquid whose infrared spectrum contains bands

$$R-O\overset{\overset{O}{\|}}{C}-Cl + R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[\text{Et}_2\text{O}]{\text{Et}_3\text{N}} R-O-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R + HCl$$

identical with those observed in the corresponding peroxide decomposition.

(c) The kinetics of the decomposition of peroxide II were measured at various pressures from 1 to 3000 kg./cm.^{2} (Table IV). A plot of ln k vs. pressure is linear from 1 to 2000 kg./cm.^{2} and the slope yields a value of ΔV^* of -5.1 cc./mole. According to evidence presented in Table III, isooctane is the least likely solvent in which the decomposition should show a negative ΔV^*, inasmuch as the yield of inversion product is lowest in this solvent at atmospheric pressure. Obviously, pressure has the expected effect of favoring the reaction with the more negative ΔV^*.[17]
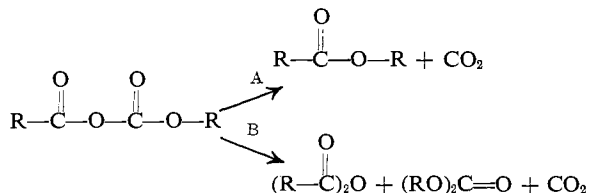
(d) The free-radical efficiencies of peroxide I are greater in carbon tetrachloride (Table I) than in

(15) A recent paper by Walling, et al., further substantiates the contention of Greene, Stein, Chu, and Vane that trans-4-t-butylcyclohexaneformyl peroxide undergoes rearrangement to an alkyl acyl carbonate: cf. C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, J. Am. Chem. Soc., 87, 518 (1965).

(16) D. S. Tarbell and E. J. Longosz, J. Org. Chem., 24, 774 (1959).

(17) Infrared spectra of the products of the decompositions under pressure show that the yields of both the inversion product and ester increase with increasing pressure. This could result if both the rearrangement of the peroxide and the subsequent decomposition of the inversion product to ester[18] had negative activation volumes.

(18) Tarbell and Longosz[16] have shown that acyl alkyl carbonates decompose thermally by two routes. Apparently the decompositions

$$R-O-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-O-R \underset{B}{\overset{A}{\displaystyle\rightarrow}} \begin{array}{l} R-\overset{\overset{O}{\|}}{C}-O-R + CO_2 \\[2em] (R-\overset{\overset{O}{\|}}{C})_2O + (RO)_2C{=}O + CO_2 \end{array}$$

of the two acyl alkyl carbonates pertinent to this discussion decomposed predominantly by path A, i.e., the corresponding esters are the main products of decompositions.
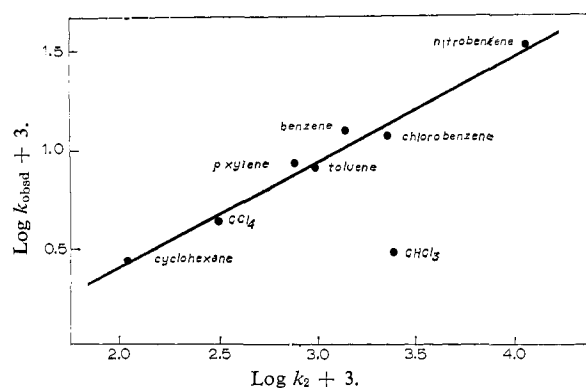
Figure 2. Plot of log $k_{\text{obsd}} + 3$ (decomposition of isobutyryl peroxide, min.$^{-1}$) vs. log $k_2 + 3$ (pyridine-t-butyl peroxyformate in 1. mole^{-1} sec.$^{-1}$, taken from Pincock, ref. 3).

benzene,[5] although carbon tetrachloride is the heavier, more viscous solvent.

Both of the inversion compounds are relatively stable in carbon tetrachloride. Isopropyl isobutyryl carbonate is sufficiently stable in some nonpolar solvents that, in the decomposition of peroxide II in those solvents, to a good approximation, none of the inversion product is destroyed in the time required to destroy all of the peroxide. Therefore, the yield of isopropyl isobutyryl carbonate can be determined by infrared analysis of solutions in which the peroxide has been destroyed by heating.

Table IV. Effect of Pressure on the Kinetics of Decomposition of Peroxide II (at 50°) in Isooctane[a,b]

Run no.	P_0, M	Pressure, kg./cm.^{2}	$10^4 k_{\text{obsd}}$, sec.$^{-1}$
1	0.09	1	1.20 ± 0.02
2	0.09	500	1.33 ± 0.02
3	0.045	1000	1.79 ± 0.02
4	0.09	1000	1.84 ± 0.02
5	0.09	1000	1.80 ± 0.01
6	0.045	2000	2.05 ± 0.01
7	0.045	3000	2.25 ± 0.02

[a] Rates measured iodometrically. Each rate constant was obtained by least-squares adjustment of five data per run to the first-order rate law. Each run was measured through 75% reaction. [b] See Acknowledgment.

Data thus obtained which are given in Table III show that the yield of the inversion product, isopropyl isobutyryl carbonate, increases with the increasing per unit volume polarizabilities of the nonpolar solvents. Since both the rate of decomposition of peroxide II and the fraction thereof which decomposes to give inversion product increase with increasing solvent polarizability, we are led to suggest that isobutyryl peroxide decomposes by two discreetly different paths, homolysis and inversion product formation. Since the yield of inversion product increases with increasing polarizability of the solvent, it is obvious that while both the transition states are somewhat polar, the transition state of the rearrangement process is more polar than is that of the homolysis.[19]

(19) (a) D. B. Denney and D. Z. Denney, J. Am. Chem. Soc., 79, 4806 (1957); (b) D. B. Denney, ibid., 78, 590 (1956); (c) J. E. Leffler and C. C. Petropoulos, ibid., 79, 3069 (1957); (d) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp. 632–634.

Table V. Decomposition Products of Peroxides I and II in Carbon Tetrachloride with BDPA[a,b]

Run no.	P_0	Z_0	RCl	RH	Alkene	RR	Alkene–CCl$_4$ adduct	Ester[c,d]	Acid[e]	Inversion product[a]	CHCl$_3$	C$_2$Cl$_6$	Temp., °C.
							Peroxide I						
7, 8	0.11	0	0.52	0.07	0.05	0.06	0.16	0.52	0.22	Not determined	0.16	0.22	35
21, 22	0.10	0.09	0.11	0.06	0.24	0.06	0	0.44	0.37	Not determined	0	0	35
1–6	0.11	0	0.59	0.07	0.08	0.06	0.14	0.47	0.17	Not determined	0.13	0.24	50
29–31	0.11	0.05	0.18	0.06	0.23	0.06	0	0.41	0.41	Not determined	0	0	50
18–20	0.10	0.09	0.11	0.07	0.24	0.06	0	0.36	Not determined		0	0	50
27, 28	0.09	0.18	0.08	0.06	0.23	0.05	0	0.40	Not determined		0	0	50
9, 10	0.11	0	0.68	0.08	0.11	0.05	0.12	0.45	Not determined		0.13	0.21	65
23, 24	0.10	0.09	0.12	0.07	0.22	0.05	0	0.38	Not determined		0	0	65
11, 12	0.11	0	0.77	0.08	0.14	0.05	0.10	0.44	Not determined		0.11	0.21	85
25, 26	0.10	0.09	0.20	0.07	0.22	0.05	0	0.41	Not determined		0	0	85
							Peroxide II						
32–36	0.09	0	0.72	Not determined		0.12	0.25	0.24	0.16	0.27	0	0.31	30
47–51	0.09	0.10	0.05	Not determined		0.06	0	0.18	0.73	0.25	0	0	30
37–41	0.09	0	0.79	0.21[e]		0.12	0.20	0.20	0.13	0.27	0	0.35	50
52–56	0.09	0.10	0.05	0.32[e]		0.06	0	0.16	0.61	0.25	0	0	50
42–46	0.09	0	0.93	Not determined		0.13	0.14	0.19	0.10	0.26	0	0.40	80
57–61	0.09	0.10	0.05	Not determined		0.07	0	0.15	0.50	0.25	0	0	80

[a] Yields reported in mole/mole of peroxide decomposed. Yields of all products except inversion product of II were determined by g.l.c. The yields of the inversion product of II were determined by infrared analysis, using its carbonyl absorption at 1805 cm.$^{-1}$; these yields probably are high, since they are based on comparison of spectra with those of an impure synthetic sample. All yields reported are averaged values from two or more determinations. [b] P_0 and Z_0 are the initial molar concentrations of peroxide and BDPA, respectively. [c] Yields of ester (from I) and acid (from I and II) were determined both by g.l.c. and by infrared analysis (using their carbonyl absorption bands). The values given are those determined by infrared analysis, but those determined by g.l.c. were all within 10% relative of the values presented. The yields of the ester from II were determined by g.l.c. only. [d] The esters were formed almost exclusively by nonradical decomposition of the inversion products. The methods of determining the inversion product yields and yields of the subsequently formed ester in the decomposition of II are discussed in the text. [e] Total yield of propene and propane.

Table V lists the decomposition products of peroxides I and II in pure carbon tetrachloride and in the same solvent containing excess BDPA. In general, the product studies were performed as follows. Two or more sample vials, after degassing and sealing, were heated at the temperatures given for a time sufficient to destroy all the peroxide. In the decomposition of peroxide II, the inversion product was sufficiently stable that its yield could be determined by infrared analysis after heating the vial for this initial heating period. Other vials were subjected to a second heating period at 100° for 2 days in order to destroy the intermediate inversion product. It was found that the heating period at the higher temperature had no discernible effect upon the yields of products other than ester.[19]

In the decomposition runs on both peroxides in pure carbon tetrachloride for which the product studies are complete, the data indicate an approximate material balance in alkyl groups. Thus, in the decomposition of cyclohexaneformyl peroxide (I), 2.10 (35°) and 2.04 (50°) C-6 alkyl groups are found in the products. Likewise, in the decompositions of isobutyryl peroxide (II) at 50°, 1.96 C-3 alkyl groups are accounted for in the products.[20] These values are not significantly different from the theoretical value of 2.

Before further discussing the products, a specific effect of BDPA upon the products should be noted.

(20) In accounting for R groups in the products of peroxide II, one may add in either the inversion product yield or ester yield, but not both. In runs 37–41 in Table V, one accounts for 2.10 or 1.96 R groups, depending upon which yield is added into the total. The higher apparent yield of inversion product could have been caused by the fact that the synthetic sample used for comparison was impure (see footnote a, Table V).

In the presence of excess BDPA, significantly higher yields of acid are formed in the decompositions of both peroxides. The following points concerning the increased acid yields should be noted.

(a) BDPA does not cause a significant effect upon the rate of decomposition of either peroxide in the concentration ranges used for the product studies (see Tables II and V). This demonstrates that the increased acid yields are not formed by direct reactions of BDPA with either peroxide.

(b) The increased acid yields are not caused by reactions of BDPA with either inversion product. In the first place, the entire acid yield formed in the decomposition of either peroxide in the presence of BDPA is formed in the early part of the reaction, during the decomposition of the peroxide itself. No additional acid is formed in the subsequent decomposition of the inversion product. This is further indicated by the fact that the yields of inversion product in decompositions of peroxide II are approximately the same in pure carbon tetrachloride and in the presence of BDPA.

(c) Experiments whose results are presented in Table VI have shown that the yield of acid in the decomposition of peroxide I is not increased in the presence of BDPA when benzene is used as solvent. However, there is a significant increase in the yield of acid in the decomposition of peroxide II in isooctane in the presence of BDPA.

These points of evidence lead us to postulate that the increased acid yields formed in the presence of BDPA result from the transformation of acyloxy radicals to acid molecules, by some unknown mechanism, by

Table VI.[a] Decompositions of Peroxides I and II at 50°

Run no.	P_0	Z_0	Alkene[b]	Acid[c]
	Peroxide I in benzene			
62, 63	0.09	0	0.32	0.14
64, 65	0.09	0.11	0.28	0.12
	Peroxide II in isooctane			
66, 67	0.05	0	Not determined	0.10
68, 69	0.05	0.1[d]	Not determined	0.35

[a] P_0 and Z_0 are the initial molar concentrations of peroxide and BDPA, respectively. [b] Determined by g.l.c. [c] Determined by infrared analysis, using the respective carbonyl stretching absorption bands of the acids. [d] Solutions made up at this formal BDPA concentration, however only a fraction of the BDPA dissolved. Resulting solutions were much less deeply colored than similar solutions of BDPA in other solvents.

BDPA. Since BDPA increases the acid yields in the peroxide decompositions without affecting the rates thereof, at least one intermediate is required. The intermediate does not appear to be inversion product or any other "stable" product which could be transformed to acid. Finally, it is for decompositions in the two solvents (carbon tetrachloride and isooctane) in which there is more homolysis (*i.e.*, least inversion product formation (see Table III)) that the effect is most pronounced.

It is not without a certain amount of trepidation that we invoke the acyloxy radical postulate to explain the effect in question, not because we lack conviction that acyloxy radicals are involved in aliphatic diacyl peroxide decompositions,[21] but rather, because of the magnitude of the effect involved. Thus, one can calculate the fraction f' of radicals which are scavenged as acyloxy radicals from the formula

$$f' = \frac{\text{increase in acid yield}}{\text{total radical yield}} = \frac{[\text{acid}]_p - [\text{acid}]_a}{2f}$$

where $[\text{acid}]_p$ and $[\text{acid}]_a$ are the yields of acid in mole/mole of peroxide decomposed in the presence and absence of BDPA, respectively. Using the data for decompositions at 50° (Tables I and V) one calculates that values of f' for both peroxides are near 0.47. Nevertheless, recent evidence which bears upon this subject lends credibility to the postulate.[22]

The yields of alkyl chlorides provide an interesting contrast in the behavior of the two peroxides. If the total radical yields $(2f)$ determined by the excess BDPA method (Table I) are correct, then, in the absence of free-radical chain chlorination reactions perpetrated by the solvent, the yield of alkyl chloride from a peroxide decomposition in the absence of scavenger should be no greater than $2f$ mole/mole of peroxide. If the alkyl chloride yield in the absence of BDPA is represented by $[\text{RCl}]_a$, then, at the temperatures for which comparisons are available for peroxide I, $2f < [\text{RCl}]_a$, while for peroxide II, $2f > [\text{RCl}]_a$.

The first of these conditions is least reasonable. A possible explanation is that all the radicals are not scavenged by BDPA in the kinetics–efficiency experiments on peroxide I conducted at low BDPA concen-

trations. However, the facts that the kinetics runs on both peroxides given in Table I showed pseudo-first-order behavior through high conversion, and that the rate constants obtained are independent of Z_0/P_0, tend to detract from this view. Chloroform is formed in the decomposition of I (but *not* II) in pure carbon tetrachloride, but it is not formed in the presence of BDPA. The presence of chloroform in the decompositions of I in carbon tetrachloride suggests that some of the initial products are chain-chlorinated by the solvent, although it is not possible to determine from the product yields which products are thus being attacked. The only product other than acid whose yield *increases* in the presence of BDPA is cyclohexene.

However, our evidence does not clearly show that the condition $2f < [\text{RCl}]_a$ can be ascribed to the chain chlorination of either cyclohexene[23] or cyclohexane by carbon tetrachloride. Thus, 3-chlorocyclohexene could be distinguished from chlorocyclohexane under the conditions used (and was undetectable in the products), and cyclohexane yields do not *increase* in the presence of BDPA. Therefore, we have no firm explanation as to the reason why $2f < [\text{RCl}]_a$ in the decomposition of peroxide I.

In general, the products of the decompositions of peroxides I and II in carbon tetrachloride other than the esters and their precursors can be attributed to reactions which have been adequately described in papers by DeTar and co-workers on decompositions of other peroxides in that solvent.[21,24] Thus, the alkenes (which are precursors of the carbon tetrachloride adducts, reported in Table V), the alkanes containing one R group, the alkane dimers (bicyclohexyl and 2,3-dimethylbutane), and the acids which are formed in decompositions in pure carbon tetrachloride probably result from free radical cage reactions, while hexachloroethane is the main termination product in both decompositions.

One difference in behavior of the two peroxides merits discussion. In the decomposition of peroxide I, the yield of RR (bicyclohexyl) does not decrease significantly in the presence of BDPA, while the yield of the corresponding compound (2,3-dimethylbutane) in the decomposition of peroxide II is diminished by a factor of 2. It is not possible to determine from the data whether the BDPA interfered with cage recombination of isopropyl radicals in these experiments,[25,26] or whether BDPA merely interferes with recombination of *free* isopropyl radicals in carbon tetrachloride.[27]

(21) D. F. DeTar and R. C. Lamb, *J. Am. Chem. Soc.*, **81**, 122 (1959).
(22) (a) H. J. Shine, J. A. Waters, and D. M. Hoffman, *ibid.*, **85**, 3613 (1963); (b) D. B. Denney, R. L. Ellsworth, and D. Z. Denney, *ibid.*, **86**, 1116 (1964).

(23) E. C. Kooyman and E. Farenhorst, *Rec. trav. chim.*, **70**, 867 (1951).
(24) (a) D. F. DeTar and C. Weis, *J. Am. Chem. Soc.*, **78**, 4296 (1956); **79**, 3041 (1957); (b) D. F. DeTar and D. V. Wells, *ibid.*, **82**, 5839 (1960).
(25) Waits and Hammond[26] have recently reported experiments on decompositions of azo-1-cyanocyclohexane and the corresponding ketenimine in the presence of scavengers (bromine, iodine, DPPH). They found that the scavengers began to interfere with cage recombination reactions at concentrations near 0.1 *M*. Since [BDPA]₀ was in this same range in experiments reported here, it is possible that BDPA interfered with cage recombination of isopropyl radicals. It was found (in experiments not reported in Table V) that further increase in [BDPA]₀ did not further diminish the yield of R–R. However, limited solubility of BDPA could be responsible for the observed threshold yield of 2,3-dimethylbutane.
(26) H. P. Waits and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1911 (1964).
(27) Our data do not completely describe the termination processes in either decomposition. Although no unidentified g.l.c. peaks were observed, we have not synthesized either of the cross-termination products, RCCl₃. If there is termination between like radicals (isopropyl and trichloromethyl), then cross termination between the two should be observed.

In either case, the isopropyl radical is apparently scavenged somewhat more readily by BDPA than is the cyclohexyl radical.

The same type of conclusion can be reached by observing the depression in the yields of RCl in the decomposition of the two peroxides which is wrought by BDPA. The isopropyl chloride yields are depressed by a greater factor under similar conditions than are the yields of cyclohexyl chloride. Thus the isopropyl radical exhibits a somewhat greater selectivity in reactivity when its reactions with BDPA and carbon tetrachloride are compared. On this basis, the isopropyl radical is somewhat more stable than the cyclohexyl radical.

A final point derives from the fact that BDPA fails to completely suppress alkyl chloride formation in decompositions of both peroxides. From the RCl yields obtained in decompositions in which $[BDPA]_0$ = 0.05–0.1 M, one can calculate that, in the kinetics–efficiency experiments (Table I) in which the BDPA concentrations used were near 5×10^{-5} M, essentially all of the alkyl radicals formed reacted with solvent rather than BDPA. This means that most of the radicals trapped in the kinetics–efficiency experiments were trichloromethyl radicals and possibly (depending upon their lifetimes) acyloxy radicals. This fact would alter neither the kinetics nor observed efficiencies, so long as BDPA at 5×10^{-5} M completely inhibits the radical termination processes which would have occurred in its absence.

Experimental[28]

The synthesis of cyclohexaneformyl peroxide has been described.[5]

Isobutyryl peroxide was prepared by the method of Kharasch, Kane, and Brown.[10] The peroxide was purified by vacuum distillation at room temperature. Iodometric titration indicated purities of 96–98% for the batches used.

Isopropyl chloroformate was obtained commercially.[29] Cyclohexyl chloroformate was prepared by a method analogous to that given by Tarbell and Longosz for other chloroformates[16]; b.p. 47° (1 mm.).

Cyclohexyl cyclohexanecarbonyl carbonate and isopropyl isobutyryl carbonate were prepared from the respective chloroformates and acids by the method of Tarbell and Longosz.[16] No suitable method for the purification of the liquid cyclohexyl cyclohexanecarbonyl carbonate could be found. The infrared spectrum shows bands at 1790 (s) and 1745 (w) cm.$^{-1}$. The isopropyl isobutyrylcarbonate was distilled under reduced pressure, b.p. 49° (1 mm.). The infrared spectrum has bands at 1805 (s) and 1760 (w) cm.$^{-1}$. The n.m.r. spectrum shows doublets at τ 8.67 and 8.79, and heptets at 7.41 and 5.08. While the n.m.r. spectrum is in qualitative agreement with the structure assumed, and is distinguishable from those of isobutyric anhydride and of isopropyl isobutyrate, the

areas of the two heptets, which may be assigned to the H—C—C=O group and the -O—C—H group, respectively, are roughly 2:1. Therefore we assume that material thus obtained is a mixture.

BDPA was prepared by the method of Koelsch,[7a] and also by the elegant method of Kuhn and Neugebauer.[7d] Mention should be made of certain difficulties encountered in the determination of the extinction coefficient of this material. When recrystallized from benzene, green, lustrous crystals are obtained which are supposedly a 1:1 benzene adduct.[7] This material, dissolved in carbon tetrachloride, gave 490 mμ (ϵ 28,900), assuming that it is a 1:1 complex. When recrystallized repeatedly from acetic acid (which does not form a complex with BDPA),[7a] a product was obtained which had an extinction coefficient of 26,000 at the same wave length. Likewise, the benzene adduct, when ground to a fine powder in an agate mortar and subsequently heated at 100° *in vacuo* for 2 hr. or subjected to vacuum for 1 day, gave a value of ϵ 26,000 assuming all the benzene had been removed. This material gave an acceptable compositional analysis.[30] Samples thus obtained, and samples recrystallized several times from acetic acid, were used in this work. The lower value of ϵ was used throughout.

Anal.[31] Calcd. for $C_{33}H_{21}$: C, 94.93; H, 5.07. Found (for sample which had been recrystallized from benzene, and the crystal benzene removed by evacuation): C, 94.80; H, 5.04.

Product Analyses. The main portion of the product analyses were determined by g.l.c. Several g.l.c. columns employed have been described,[32] and designated A–E. In addition, the following columns were used: column F, a 12 ft. $\times$ 0.25 in. column packed with 30% diethylene glycol succinate on C-22 firebrick; column G, a 6 ft. $\times$ 0.25 in. column packed with 30% Carbowax 1000 on C-22 firebrick; and column H, a 6 ft. $\times$ 0.25 in. column packed with 30% dimer acid–Silicone 550 on Neutraport-S. For brevity, Table VII

Table VII. Columns Used for G.l.c. Product Analyses[a]

Product	Peroxide I	Peroxide II
RCl	F (70°)	F (70°)
RH	F (70°)	A (70°)
Alkene	F (70°)	A (70°)
R–R	F (130°)	F (70°)
Alkene–CCl₄ adduct	F (130°)	F (130°)
Ester	F (190°)	A (130°)
Acid	H (160°)	F (130°)
CHCl₃	F (70°)	. . .
C₂Cl₆	F (130°)	F (130°)

[a] Temperatures given are the temperatures at which the column was operated for the g.l.c. analysis.

indicates the columns used for each product determined. Each product was determined by comparison of peak areas with those of standard solutions of authentic samples.

(28) A line-operated Beckman DU spectrophotometer, equipped with a specially built box-like cover for the cell chamber, was used for measuring stable radical concentrations spectrophotometrically. A Perkin-Elmer Model 421 infrared spectrophotometer was used in kinetics runs determined by infrared analysis. A Beckman GC-2 gas chromatograph was used in the products study. N.m.r. spectra were taken on a Varian A-60 spectrometer in deuteriochloroform with tetramethylsilane as an internal standard.

(29) Obtained from Chemetron Chemicals, New York, N. Y.

(30) This does not necessarily indicate that all the benzene has been removed from the crystals, for the theoretical compositions of BDPA and the 1:1 benzene complex differ little.

(31) Determined by Midwest Microlabs, Indianapolis 40, Ind.

(32) Paper II in this series: R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963).

The C-3 hydrocarbons were determined by inserting decomposition vials equipped with break-seal directly into the helium line at the inlet of the g.l.c. instrument. Since carbon dioxide was found to interfere, a quantity of Ascarite was placed between the vial and the g.l.c. inlet.

Cyclohexanecarboxylic acid and isobutyric acid were determined quantitatively both by g.l.c. and infrared analysis, using their carbonyl stretching absorption bands at 1695 and 1700 cm.$^{-1}$. Both acids were identified qualitatively by comparison of the infrared spectra of authentic samples with those of samples which had been obtained by extraction of decomposition mixtures with 10% sodium bicarbonate solution.

Kinetics Runs. The procedures used in the regular kinetics runs have been described.[5]

The high-pressure equipment employed in these experiments consisted of three main components: a commercial hydraulic hand pump (Blackhawk P-39), a high-pressure intensifier unit, and a reaction autoclave. The intensifier unit and autoclave were of standard design (see Acknowledgment). The autoclave was immersed in an oil bath whose temperature was controlled to ±0.05°. The intensifier allowed a maximum working pressure of 10,000 kg./cm.^{2}.

For the reactions under pressure, carefully degassed samples were transferred to 5-ml. syringes under a nitrogen atmosphere. After filling, each syringe was capped and placed in the autoclave (hexane was used as the pressure transmitting fluid in the autoclave). After its heating period, the pressure was released, and the syringe was removed. A portion of the sample was subsequently weighed and assayed iodometrically.

The Self-Reactions of *t*-Butylperoxy Radicals

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The self-reactions of t-butylperoxy radicals were studied by e.s.r. techniques. It was found that the reaction $2RO_2\cdot \rightarrow 2RO\cdot + O_2$ has an activation energy of 15.5 ± 1.3 kcal./mole and in benzene proceeds five times as rapidly as the reaction $2RO_2\cdot \rightarrow ROOR + O_2$ at 22°. The latter reaction appears to be the normal chain-terminating step in systems where t-butoxy radical can readily regenerate the peroxy radical. It has a rate constant in benzene of 3.9 ± 0.5 × 10^2 l. mole^{-1} sec.$^{-1}$ at 22° and an activation energy of 10.2 ± 1 kcal./mole. The data are suggestive that these two reactions proceed via the fast equilibrium, $RO_2\cdot + RO_2\cdot \rightleftarrows ROOOOR$, involving the tetroxide as an intermediate, although the evidence is not conclusive. If the tetroxide mechanism is correct, it is suggested that the chain-terminating reaction will yield oxygen in the excited $^1\Delta_g$ or $^1\Sigma_g{}^+$ states rather than the normal $^3\Sigma_g{}^-$ ground state to avoid change in multiplicity.

One of the most intriguing problems in free-radical chemistry concerns the detailed mechanism of the self-reactions of tertiary alkylperoxy radicals. Among the reactive radicals which are important intermediates in the oxidation of hydrocarbons, they show uniquely long lifetimes, reflecting a relatively slow self-reaction resulting in radical chain termination. While iodine atoms and methyl radicals exhibit diffusion limited bimolecular association rate constants in solution of about 10^{10} l. mole^{-1} sec.$^{-1}$ and the secondary tetralylperoxy radical exhibits a bimolecular chain termination rate constant of about 10^7 l. mole^{-1} sec.$^{-1}$, the rate constant of the much studied cumylperoxy radical is about 10^5 l. mole^{-1} sec.$^{-1}$, and, as discussed in this paper, the value for *t*-butylperoxy radicals is in the order of 10^3 l. mole^{-1} sec.$^{-1}$. In the former cases the activation energies are essentially nil.

It is thoroughly established from many studies that chain termination in autoxidation reactions is second order in peroxy radical concentration. *A priori* this does not necessarily mean that self-reaction constitutes a radical destroying process in itself. It does imply, however, that the self-reaction is, or is directly related to, the rate-controlling process leading to a termination event.

Detailed study of cumene autoxidation by product analysis[1] and isotopic oxygen exchange[2] demonstrate that a frequent primary step must involve the head-to-head interaction product, ROOOOR or its nonbonded equivalent, either as a transition state or as an unstable intermediate. The isotopic exchange experiments of Bartlett and Traylor show that for every chain-terminating event at 60° cumylperoxy radicals interact several times without chain termination as in reaction 1. Bartlett and Traylor were unable to

$$2RO_2\cdot \longrightarrow 2RO\cdot + O_2 \qquad (1)$$
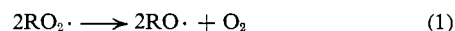
specifically define the chain-termination process in their studies, but suggested a variety of interactions involving fragmentation species of the cumyloxy radical.

(1) H. S. Blanchard, *J. Am. Chem. Soc.*, **81**, 4548 (1959).
(2) P. D. Bartlett and T. G. Traylor, *ibid.*, **85**, 2407 (1963).