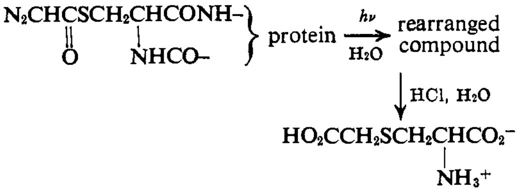

$$\left.\begin{matrix}N_2CH\underset{\overset{\|}{O}}{C}SCH_2\underset{\underset{NHCO-}{|}}{C}HCONH- \\ \end{matrix}\right\}\text{protein} \xrightarrow[H_2O]{h\nu} \text{rearranged compound} \xrightarrow{HCl,\ H_2O} HO_2CCH_2SCH_2\underset{\underset{NH_3^+}{|}}{C}HCO_2^- \qquad (10)$$

Similar rearrangement to a neighboring sulfur atom was reported by Robson and Shechter[24] in the reaction (presumably by way of a diazo compound and the corresponding carbene) of 2-ethylmercaptoacetophenone *p*-tosylhydrazone.

Migration to sulfur, in preference to insertion into water, may well be expected from carbenes. However, it was also anticipated that the migration would be greater for an amide than for an ethyl ester and greater for an ethyl ester than for a phenyl ester, on the basis of qualitative ideas of the relative availability of electrons on these atoms. Such was not the fact. We have not yet understood the reasons why the percentage of rearrangement in the compounds here studied proved essentially independent of structure, and the results may be, in part, an artifact arising from differences in experimental conditions for the various photolyses. Prior work with ethyl trifluoroacetyldiazoacetate had yielded the products of attack on solvent, rather than those of rearrangement,[25] and these results had been generalized to suggest that alkoxy groups do not migrate in Wolff-type rearrangements of diazo esters.[26] It now appears probable that the particular choice of diazo ester controlled the results obtained. Many experiments have been conducted on the photolysis of ethyl diazoacetate[27] in nonpolar solvents, but in these experiments the products of insertion into C–H bonds were deliberately sought, and the ketene (if indeed it is formed under the experimental conditions of these reactions) would not easily have been found. Insertion into the C–H bond of methanol has here been detected as a minor product in the photolysis of ethyl diazoacetate in this polar solvent. The result is significant, since it encourages us to continue the search for C–H insertion products in the photolysis of diazoacetylchymotrypsin and other diazoacetylated enzymes. Such insertions, if found, would provide a welcome, and at present unique, means of marking the hydrophobic residues near the active sites of enzymes.

It must then be concluded that the analog of a photochemical Wolff rearrangement does indeed occur to a limited extent with diazo esters, but that it is restricted (at least in diazo esters) to compounds that do not carry strongly electronegative groups. Kaplan and Meloy[28] raise the question as to whether the products of the decomposition of diazo ketones are influenced by the conformation of the compounds. The application of their idea to the photochemistry here outlined is not straightforward, but deserves investigation.

The mechanism of the photolysis of methyl phenoxyacetate has not yet been elucidated. But the products formed are analogous to those obtained in low yield in the thermal reaction of acetyl peroxide with phenols,[29] and this fact suggests that the reaction proceeds by a free-radical process.

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(24) J. H. Robson and H. Shechter, *J. Am. Chem. Soc.*, **89**, 7112 (1967).

(25) F. Weygand, H. Dworschak, K. Koch, and St. Konstas, *Angew. Chem.*, **73**, 409 (1961).

(26) P. A. S. Smith in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers New York, N. Y., 1963, p 560.

(27) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **78**, 4947 (1956); **83**, 1989 (1961).

(28) F. Kaplan and G. K. Meloy, *ibid.*, **88**, 950 (1966).

(29) F. Wessely and E. Schinzel, *Monatsh.*, **84**, 969 (1953).

The Decomposition of Peroxy Esters. II. The Photolysis of Esters of Aliphatic Peroxycarboxylic Acids

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Abstract: Photolysis of the long-chain aliphatic peroxy esters, *t*-butyl peroxycaprate and *t*-butyl peroxylaurate, in the pure liquid state was carried out at 30° with 2537 Å ultraviolet radiation. The principal products formed were carbon dioxide, capric or lauric acid, *t*-butyl alcohol, methane, and acetone. The quantum yield for each of these products was independent of the intensity of the radiation. The magnitude of the quantum yields for the decomposition of the peroxy esters and the inhibiting effect of oxygen indicate that some induced decomposition takes place in addition to the photochemical decomposition.

The thermal decomposition of aliphatic peroxy esters, RCOOOR′, where both R and R′ are alkyl groups, has been the subject of several investigations.[1] The importance of reactions of *t*-butyl peroxy esters, such as *t*-butyl peroxyacetate, with many classes of compounds in the presence of catalytic amounts of copper ions to produce well-defined acyloxy derivatives has been demonstrated.[2] Although Sosnovsky[3] has shown that those peroxy ester reactions are aided by

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(1) See, for example: (a) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958); (b) N. A. Milas and A. Golubović, *ibid.*, **80**, 5994 (1958); (c) L. J. Durham, L. Glover, and H. S. Mosher, *ibid.*, **82**, 1508 (1960); (d) R. E. Pincock, *ibid.*, **84**, 312 (1962); (e) M. Trachtman and J. G. Miller, *ibid.*, **84**, 4828 (1962); (f) P. D. Bartlett and H. Minato, *ibid.*, **85**, 1858 (1963); (g) P. D. Bartlett and L. B. Gortler, *ibid.*, **85**, 1864 (1963); (h) J. R. Shelton and H. G. Gilde, *J. Org. Chem.*, **29**, 482 (1964).

(2) G. Sosnovsky and S.-O. Lawesson, *Angew. Chem. Intern. Ed. Engl.*, **3**, 269 (1964).

(3) G. Sosnovsky, *J. Org. Chem.*, **28**, 2934 (1963); *Tetrahedron*, **21**, 871 (1965).

exposure to ultraviolet radiation which causes the reactions to take place at lower temperatures, he made no study of the effect of the ultraviolet light on the peroxy esters themselves. Walling and Gibian[4] have shown that *t*-butyl peroxyacetate undergoes photosensitized decomposition in the presence of benzophenone, but they did not study the photodecomposition of the peroxy ester alone.

The work reported here on the photolysis of two peroxy esters, *t*-butyl peroxycaprate and *t*-butyl peroxylaurate, is the first study of the photolysis of aliphatic peroxy esters. It is part of our systematic investigation of the decomposition of peroxy esters. The peroxy esters were studied neat in order to avoid the participation of solvent in the reactions.[2]

Experimental Section

Materials. Petroleum ether from J. T. Baker and Co. was washed with concentrated sulfuric acid until no discoloration of the acid occurred. The ether was then washed with sodium bicarbonate solution and finally with distilled water. It was dried over anhydrous magnesium sulfate and fractionally distilled. The fraction boiling at 50° (760 mm) was retained for use.

Pyridine, obtained from the Fisher Scientific Co., was distilled over barium oxide through a 12-in. column packed with glass helices. The fraction boiling at 115° (760 mm) was used. The pyridine was distilled immediately before use to prevent absorption of moisture from the air.

Methyl alcohol from J. T. Baker and Co. was used without further purification. Oxygen from the Matheson Co. was passed through a drying tube containing Drierite to remove any water vapor present in it. Thionyl chloride was obtained from the Fisher Scientific Co. and was used without further purification.

The *t*-butyl hydroperoxide was Lucidol Corp. material and was fractionally distilled. The fraction boiling at 45° (18 mm) and assaying 99% or better by iodometric analysis[5] was retained for use.

Capric and lauric acids were obtained from Eastman Kodak Co. and were freed from homologs in the following way. The methyl esters of the acids were prepared using an excess of methanol and sulfuric acid. After the reaction, the sulfuric acid and excess methanol were removed by extraction with water. The esters were distilled under vacuum through a 36-in. column packed with glass helices.

The purity of the methyl esters was determined by gas chromatography. The column used for the detection of homologs was a Perkin-Elmer general purpose *R* column. The temperature of the column was 225°, and a gauge pressure of 10 psi was used. In all cases, only one large peak and a small peak which amounted to only a few tenths per cent impurity were observed. The physical constants of the methyl esters are listed in Table I.

Table I. Physical Properties of the Methyl Esters

Ester	Bp, °C (mm)	n^{30}_{D} Obsd	Lit.[a]
Caprate	115.0 (15)	1.4221	1.4217
Laurate	143.0 (16)	1.4280	1.4275

[a] K. F. Mattil and H. E. Longenecker, *J. Am. Oil Chemists' Soc.*, **21**, 16 (1944).

The methyl esters were saponified by the usual laboratory procedures, and the pure fatty acids were obtained. The acyl chlorides were prepared by reacting the fatty acids with thionyl chloride.[6] The acyl chlorides were distilled *in vacuo* and retained for use in the preparation of the *t*-butyl peroxy esters.

Preparation of *t*-Butyl Peroxy Esters. The peroxy esters were prepared by the pyridine-acylation method developed by Silbert and Swern.[7] After preparation, they were washed with 0.05 *M* sodium hydroxide followed by distilled water and were then dried over magnesium sulfate. Their purity was determined by the iodometric procedure of Silbert and Swern.[5] The purity of the compounds used in this work is shown in Table II.

Table II. Physical Properties of *t*-Butyl Peroxy Esters

Peroxy ester	n^{30}_{D}		Oxygen, %		Purity, %
	Obsd	Lit.[7]	Calcd	Found	
Peroxycaprate	1.4292	1.4293	6.55	6.49	99.1
Peroxylaurate	1.4332	1.4333	5.87	5.83	99.2

Apparatus. The light source was a low-pressure mercury resonance lamp constructed for our work by the Hanovia Corporation. The lamp was in the shape of a four-coil helix which was 12.5 cm in diameter and 10.5 cm long. Approximately 90% of the output was at 2537 Å with small intensities at longer wavelengths. Corning 9-54 filters were used to remove radiation below 2200 Å. Uranyl oxalate and potassium ferrioxalate were employed as actinometers. At full intensity, both of the peroxy esters absorbed 100% of the incident radiation and the intensity was found to be 1.61 × 10^{16} quanta cc^{-1} sec^{-1} as calculated by the principle of equivalent optical densities.[8] Separate experiments using a 0.20% solution of 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene perchlorate[9] to filter out the small amount of 2967- and 3130-Å radiation present showed no change in the quantum yields, thereby proving that the source was effectively monochromatic.

All photolyses were carried out in a quartz cell equipped with magnetic stirring and a quartz water jacket used to keep the cell contents at 30 ± 0.1°. The volume of the photolysis cell[10] was 3.4 ml. Lower incident intensities of light were obtained by surrounding the cell with copper screening of different mesh sizes.

The spectrum of *t*-butyl peroxylaurate as the pure liquid and in solution in cyclohexane showed two absorption bands in the quartz ultraviolet. The lower energy band lay at 2700 Å (ϵ_{max} ~50) and the other at 2170 Å (ϵ_{max} ~80). The exciting light in the photochemical experiments (2537 Å) must result in excitation of both the higher and lower energy systems. A rough lower limit for the fraction of the incident quanta that are absorbed into the lower energy state was fixed at 0.5 by approximate extrapolations of the two observed absorption curves. We are indebted to Professor Robin M. Hochstrasser for measuring the spectrum of the pure peroxy ester and for his analysis of the spectra.

Procedure. In all experiments, the peroxy esters were first degassed by a freeze–thaw procedure. The freeze–thaw cycle was repeated at least seven times to ensure complete degassing. In some of the experiments, oxygen was added after degassing, and the photolysis cell was sealed under an oxygen pressure slightly greater than 1 atm.

After warming to room temperature, the reaction vessel was put in position in the center of the radiation helix. Photolysis times ranged from 0.5 to 2.0 hr, corresponding to 2 to 10% photolysis. After the irradiation, the photolysis cell was sealed through a break seal to a Newton flask and trapping train connected to a vacuum system. When the traps were brought to 10^{-5} torr and liquid-nitrogen temperature, the break seal was broken, and the gaseous products were collected. Trap-to-trap distillation was employed for the separation of the products into three fractions which were finally separately transferred to a pressure–volume apparatus by a Toepler pump. After pressure–volume measurements, the three fractions were collected in separate bulbs and analyzed using a Consolidated Electrodynamics Corp. 21-130 mass spectrometer for the methane (no carbon monoxide or hydrogen was produced in the photolyses) and a Burrell K-1 gas chromatograph for the other products. Samples from the gas chromatographic separation were also analyzed on the mass spectrometer to certify their identity.

The fatty acid formed as product was analyzed by titration of the undecomposed peroxy ester with sodium hydroxide. Thin film

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(4) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3413 (1965).

(5) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

(6) A. W. Ralston, E. W. Segebrecht, and S. T. Bauer, *J. Org. Chem.*, **4**, 502 (1939).

(7) L. S. Silbert and D. Swern, *J. Am. Chem. Soc.*, **81**, 2364 (1959).

(8) I. M. Claesson, *Arkiv Kemi*, **10**, 1 (1956); D. H. Volman and J. C. Chen, *J. Am. Chem. Soc.*, **81**, 4141 (1959).

(9) M. Kasha, *J. Opt. Soc. Am.*, **38**, 429 (1948).

(10) For details, see W. H. Simpson, Ph.D. Dissertation, University of Pennsylvania, 1967.

chromatography was used for qualitative analysis of other liquid products.

Separate runs were made to determine the quantum yields for the consumption of the peroxy esters both in the absence and presence of oxygen. In these runs the amount of unconsumed peroxy ester was estimated by the same iodometric procedure as used in the purity determinations.

Results and Discussion

The principal products of the photolytic decomposition of the two peroxy esters were methane, carbon dioxide, *t*-butyl alcohol, acetone, lauric acid, and capric acid (Table III). Isobutylene oxide was produced in appreciable amount by 2 hr of photolysis. Each of the values given in Table III is an average value obtained from three or more determinations.

Table III. Product Yields for the Photolytic Decomposition of the *t*-Butyl Peroxy Esters under Full Intensity of Radiation at 30°

Product	Time, hr 0.5	1	1.5	2.0	Av quantum yield
Micromoles Produced from Peroxylaurate					
Methane	1.0	2.5	4.5	6.0	0.01
Carbon dioxide	163	337	495	648	1.01
Lauric acid	95	190	289	375	0.58
t-Butyl alcohol	71	155	237	330	0.47
Acetone	3.5	6.5	10.6	15.1	0.02_2
Isobutylene oxide	*a*	*a*	*a*	6.6	...
Micromoles Produced from Peroxycaprate					
Methane	1.2	2.3	3.5	5.1	0.01
Carbon dioxide	150	315	481	647	0.96
Capric acid	67	130	195	256	0.40
t-Butyl alcohol	87	185	273	358	0.55
Acetone	4.4	8.5	12.9	15.2	0.02_6
Isobutylene oxide	*a*	*a*	*a*	6.4	...

[a] Not determined.

Small amounts of nonane and undecane were found in the liquid fraction from the decomposition of the peroxycaprate and peroxylaurate, respectively. Further analysis, by thin layer chromatography, infrared spectroscopy, and mass spectrometry, of the liquid fraction from the decomposition of the peroxylaurate showed the presence of material tentatively identified as *t*-butyl undecyl ether and a resinous substance of molecular weight 239.

The data in Table III show that the two peroxy esters decompose in the same way. Plots of product yield against time for these data are good straight lines for all of the products. A representative plot is given in Figure 1 for the production of carbon dioxide and *t*-butyl alcohol in the decomposition of *t*-butyl peroxylaurate. The linearity indicates that the products have no important effect on the absorption of light by the peroxy esters in the time interval studied.

The absence of photolysis of the products was also demonstrated by the fact that no carbon monoxide was found from possible photolysis of the acetone. Furthermore, the quantum yields of the major products were found to be independent of the intensity of the radiation as shown in Table IV.

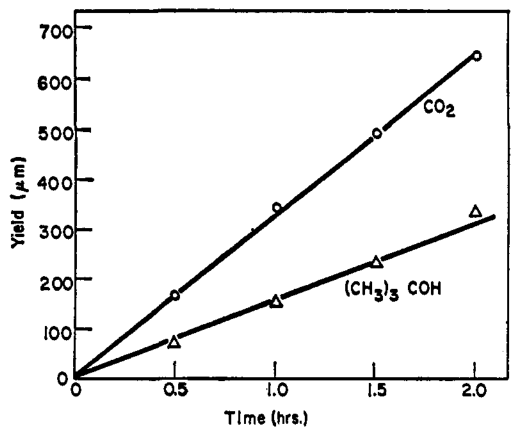

Figure 1. Yield of CO_2 and $(CH_3)_3$ COH *vs.* time in the photolysis of *t*-butyl peroxylaurate.

Table IV. Quantum Yields of the Principal Products from *t*-Butyl Peroxylaurate at Different Intensities

Product	Quantum yield[a] I_1	I_2	I_3
Methane	0.01	0.01	0.01
Carbon dioxide	1.01	0.95	0.95
Lauric acid	0.58	0.47	0.55
t-Butyl alcohol	0.47	0.53	0.52
Acetone	0.02	0.02	0.02

[a] $I_1 = 1.61 \times 10^{16}$ quanta cc^{-1} sec^{-1}, $I_2 = 4.36 \times 10^{15}$ quanta cc^{-1} sec^{-1}, and $I_3 = 9.10 \times 10^{15}$ quanta cc^{-1} sec^{-1}.

The quantum yield of decomposition, ϕ_d, was 1.52 for the peroxycaprate and 1.76 for the peroxylaurate. The value of ϕ_d fell to 1.16 when oxygen was added to the peroxylaurate. The high values for the degassed samples and the decrease in the presence of oxygen are evidence that some induced decomposition of the peroxy esters takes place. Bartlett, Benzing, and Pincock[11] found that the small amount of oxygen present due to the air dissolved in the ether used as solvent exerted a great inhibition on the induced decomposition of di-*t*-butyl peroxyoxalate. It is interesting that the thermal decomposition of *t*-butyl peroxycaprate in chlorobenzene at 110° showed[1e] no induced decomposition by its kinetics and produced no isobutylene oxide.

Although plausible reactions can be written to account for all of the products obtained, no definite mechanism can be given at present for the photolysis of the peroxy esters. More information concerning the primary process is required, especially because the spectrum of the peroxylaurate indicates that in our experiments the radiation was absorbed into both the carbonyl $n\pi^*$ state and the O–O group continuum. The nature of the induced reaction must also be studied more completely.

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