amino acids may be expected to have analogies in CI mass spectrometry (*viz.*, $QM^+ - COOH_2$ and $QM^+ - H_2O$) but important CI processes (*e.g.*, α,β fission, etc.) may be unknown or obscure in solution chemistry.

Rearrangement processes so prevalent in the EI mass spectra of amino acids[6–8] and their derivatives[9–11] are generally absent from the CI mass spectra probably because of the even-electron character of the ions as well as the possibility of their dissipating excess energy through collision processes. While rearrangement ions in EI mass spectra may provide considerable structural information when the mechanism of their formation is well understood, they may cause considerable confusion when their origin is unclear. It is therefore both a strength and a weakness of CI mass spectra that few rearrangements are encountered.

It seems highly artificial to consider the CI technique as an alternative rather than as a complement to EI mass spectrometry since merely stopping the reagent gas flow into the source permits a rapid return to EI conditions. It is clear that both spectra have advantages and disadvantages and in application to a genuine problem the combination of both methods will be most advantageous.

Experimental Section

The amino acids used in this work were all Mann assayed amino acids.[20] Mass spectra were measured at low resolving power on an MS-902 using the dual EI/CI source described previously.[3] All spectra were measured at a source temperature of 250 ± 5°.

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[20] Mann Research Laboratories, Inc., New York, N. Y. 10006.

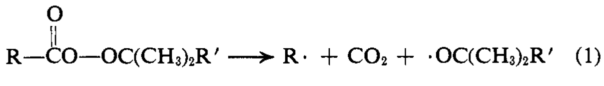
Photolysis of Peresters. Reactions of Alkoxy–Alkyl Radical Pairs in Solution

Roger A. Sheldon and Jay K. Kochi

Contribution No. 1851 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. Received November 8, 1969

Abstract: A series of peresters $RCO_2OC(CH_3)_2R'$ cleanly liberate 1 mol of carbon dioxide with a quantum yield of unity when irradiated in solution at 2537 Å. An alkyl radical $R\cdot$ and an alkoxy radical $\cdot OC(CH_3)_2R'$ are the first discernible intermediates. The electron spin resonance spectrum of the alkyl radical $R\cdot$ is obtainable when photolyses are carried out directly in the cavity of the spectrometer. The esr spectrum of $R'\cdot$ from the secondary fragmentation of the alkoxy radical is readily observed with isopropyl, *t*-butyl, and benzyl simultaneously with its partner $R\cdot$ at −115°, but is not seen when R′ is methyl or ethyl. Reactions of the alkyl–alkoxy radical pair are considered to proceed from a solvent cage. Combination to form ether $ROC(CH_3)_2R'$ and disproportionation to alcohol $R'(CH_3)_2COH$ and alkene R(–H) are exclusively cage processes. The relative rates of disproportionation and combination k_d/k_c for alkyl–alkoxy and alkyl–alkyl radical pairs are compared and discussed in terms of the transition state for disproportionation. The yield of ether from *t*-butyl peracetate can be quantitatively related to the efficiency of the cage process in a series of solvents. Cage reactions in the thermal and photochemical decomposition of peresters are qualitatively compared. Examination of the rearrangement of cyclopropylmethyl radical leads to an estimate of 10^9 sec^{-1} for the combination of an alkyl and an alkoxy radical pair.

Peresters are useful as free radical precursors because the thermal decomposition[1] represented in eq 1 is



$$R-\overset{\overset{O}{\|}}{C}O-OC(CH_3)_2R' \longrightarrow R\cdot + CO_2 + \cdot OC(CH_3)_2R' \quad (1)$$

less complicated by competing heterolytic processes such as carboxy inversion[2] than it is with diacyl peroxides. The photochemical decomposition of *t*-butyl percaprate and perlaurate as pure liquids produced carbon dioxide with a quantum yield of unity (at 2537 Å) and other products derived from free radical intermediates.[3] The high quantum yield for decomposition (Φ = 1.5–1.8) and the formation of isobutylene oxide and carboxylic acid, however, indicated that induced decomposition was also occurring under these conditions. The photosensitized decomposition of *t*-butyl peracetate has also been reported.[4]

Direct photolysis of aliphatic peresters in solution was recently shown to be a useful method of generating alkyl radicals for electron spin resonance (esr) studies.[5,6] In conjunction with these esr results we now wish to report a product study from the photolysis of a series of aliphatic peresters with the following objectives: (a) correlation of the esr results with the products of photolysis; (b) determination of the efficiency of the photoinduced homolytic decomposition; (c) assessment of the competition from heterolytic processes and the comparison with thermolytic decomposition; (d) delineation of possible reactions of alkyl–alkoxy

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(1) See for example: (a) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, 80, 1398 (1958), and subsequent papers in this series; (b) N. A. Milas and A. Golubovic, *ibid.*, 80, 5994 (1958); (c) M. Trachtman and J. G. Miller, *ibid.*, 84, 4828 (1962); (d) Y. K. Syrkin and I. I. Moiseev, *Russ. Chem. Rev., Engl. Trans.*, **29**, 163 (1960).

(2) (a) P. D. Bartlett and T. G. Traylor, *J. Amer. Chem. Soc.*, 83, 856 (1961); (b) R. Criegee and R. Kaspar, *Ann.*, 560, 127 (1948); (c) E. Hedaya and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1661 (1967).

(3) W. Simpson and J. Miller, *ibid.*, **90**, 4093 (1968); also *cf.* L. A. Singer and N. P. Kong, *ibid.*, 88, 5213 (1966), and E. N. Cain, R. Vukov, and S. Masamune, *Chem. Commun.*, 98 (1969).

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

(5) J. Kochi and P. Krusic, *ibid.*, **91**, 3940 (1969).

(6) P. Bakuzis, J. Kochi, and P. Krusic, *ibid.*, **92**, 1434 (1970).

Table I. Ultraviolet Absorption of Peresters at 2537 Å in *n*-Hexane

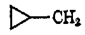
Perester $RCO_2OC(CH_3)_2R'$ R	R'	ε, M^{-1} cm^{-1}	Perester $RCO_2OC(CH_3)_2R'$ R	R'	ε, M^{-1} cm^{-1}
CH_3	CH_3	21		CH_3	20
CH_3	CH_2CH_3	20		CH_3	30
CH_3	$CH(CH_3)_2$	23	$(CH_3)_3C$	CH_3	38
CH_3CH_2	CH_3	28	$(CH_3)_3C$	CH_2CH_3	43
CH_3CH_2	CH_2CH_3	27	$(CH_3)_3C$	$CH(CH_3)_2$	41
$(CH_3)_2CH$	CH_3	26	$(CH_3)_3COOC(CH_3)_3$		8

Table II. Photolysis of Peresters $RCO_2OC(CH_3)_2R'$ in Decalin Solutions at 2537 Å[a]

Perester R	R'	mmol	CO_2[b]	RH	R-(–H)	R'H	R'(–H)	R–R	R'–R'	R–R'	Alco-hol[c]	Ether[d]	Dmk[e]	ΣR[f]/CO_2
CH_3	CH_3	0.54	0.52 (96)	0.26						t[g]	0.25	0.23	t	0.94
CH_3CH_2	CH_3	0.51	0.48 (94)	0.21	0.06	t		t		t	0.27	0.19	t	0.96
$(CH_3)_2CH$	CH_3	0.51	0.50 (98)	0.11	0.24	t		~0.01		t	0.37	0.10	t	0.90
$(CH_3)_3C$	CH_3	0.52	0.50 (96)	0.065	0.37	t		~0.01			0.45	0.02	t	0.91
CH_3	CH_2CH_3	0.51	0.49 (96)	0.24		0.03	None	None		~0.01	0.22	0.21	0.04	0.92
CH_3CH_2	CH_2CH_3	0.54	0.50 (92)	0.25	0.06			t		~0.01	0.28	0.18	0.04	1.00
$(CH_3)_2CH$	CH_2CH_3	0.52	0.51 (98)	0.10	0.18	0.03	None	~0.01		t	0.36	0.10	0.04	0.77
$(CH_3)_3C$	CH_2CH_3	0.50	0.45 (90)	0.08	0.27	0.03	None	~0.01	t	t	0.37	~0.01	0.03	0.82
CH_3	$CH(CH_3)_2$	0.52	0.48 (92)	0.28		0.13	0.06	None	~0.01	0.03	0.09	0.14	0.22	0.94
CH_3CH_2	$CH(CH_3)_2$	0.53	0.52 (98)	0.29	0.03	0.14	0.06	t	~0.01	0.04	0.11	0.12	0.22	0.92
$(CH_3)_2CH$	$CH(CH_3)_2$	0.51	0.50 (98)	0.23	0.16					0.08	0.22	0.06	0.18	1.06
$(CH_3)_3C$	$CH(CH_3)_2$	0.50	0.46 (92)	0.10	0.23	0.10	0.05	t	~0.01	~0.01	0.27	~0.01	0.16	0.77
Ph	CH_3	0.50	0.32[h] (64)	0.17				None	None	None	0.34	0.14	None	

[a] In solutions containing 5 ml of decalin and approximately 0.5 mmol/ester at 30°. All runs in duplicate. All yields expressed as mmoles; t = traces found. [b] Number in parentheses is yield of CO_2 based on perester charged. [c] $R'C(CH_3)_2OH$. [d] $R'C(CH_3)_2OR$. [e] Acetone. [f] ΣR includes all products derived from R·. [g] Traces ($\gtrsim$0.01 mmol). [h] Benzoic acid (0.15 mm) was formed.

radical pairs; (e) determination of the extent and the nature of the cage reactions; and (f) fragmentation of alkoxy radicals. In this study the photochemical processes *per se* have not been our principal concern, and we hope to present the photochemistry at a later time.

Results and Discussion

Peresters like diacyl peroxides[7] have continuous weak absorption in the ultraviolet region beginning around 2800 Å due to the n–π* transition in the carbonyl group[8] and the peroxide continuum[9] (Table I).

The Stoichiometry. A series of *t*-alkyl peresters of the general structure $RCO_3C(CH_3)_2R'$ (R,R' = CH_3, CH_3CH_2, $(CH_3)_2CH$, $(CH_3)_3C$) were irradiated at 2537 Å in *n*-pentane, decalin, and acetonitrile solutions (0.1 *M*) at 30°. Carbon dioxide (1 mol) was cleanly formed (>90%) with a quantum yield of unity (see Experimental Section), in agreement with results previously obtained with the neat perester.[3] However, no carboxylic acid was found by gas chromatographic analysis. The remainder of the material balance was quantitatively accounted for as alkane (RH, R'H), alkene [R(–H), R'(–H)], *t*-alcohol [$R'(CH_3)_2COH$], *t*-alkyl ether [$R'(CH_3)_2COR$], acetone, and mixed alkyl dimer (R–R') as shown in Table II. Comparative studies were also carried out in *n*-pentane and acetonitrile as solvents of contrasting polarity. The results are given in Table III. Higher yields of acetone and products (R'–R' and R–R') derived from R'· were apparent in acetonitrile.

$$RCO_2OC(CH_3)_2R' \longrightarrow \begin{cases} RH,\ R(-H),\ ROC(CH_3)_2R' \\ CO_2\ [\phi = 1] \\ R'H,\ R'(\text{-}H),\ (CH_3)_2CO,\ R'(CH_3)_2COR \end{cases} \qquad (2)^{10}$$

The photolysis of *t*-butyl perbenzoate unlike the aliphatic analogs afforded only a 64% yield of carbon dioxide and a significant amount (30%) of benzoic acid. Benzene and *t*-butyl phenyl ether were the other products.

A large number of pathways are available for the formation of products in the photolysis of peresters. The stoichiometric relationships among these products are given in Table IV for decompositions carried out in decalin. The important features of this table are: (a) the high material balance of products derived from the alkyl (R–) and alkoxy [$R'(CH_3)_2CO$–] fragments relative to the carbon dioxide liberated (columns 2 and 6); (b) the decrease in the alcohol–acetone ratio in the series: R' = methyl < ethyl < isopropyl (column 9); (c) the increase in the alcohol–ether ratio in the series: R = methyl < ethyl < isopropyl < *t*-butyl (column 3); (d) the alcohol–{ether + alkene [R(–H)]} ratio remains almost constant through this series of *t*-butyl, *t*-amyl, and 2,3-dimethyl-2-butyl peresters (column 4).

The good material balances obtained in most cases indicate that no significant products were missed in the analysis. Products derived from reaction between

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(7) See R. Sheldon and J. Kochi, *J. Amer. Chem. Soc.*, **92**, 4395 (1970).

(8) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, pp 366 ff.

(9) L. M. Dorfman and Z. W. Salsburg, *J. Amer. Chem. Soc.*, **73**, 255 (1951); D. H. Volman and W. M. Graven, *ibid.*, **75**, 3112 (1953); ref 8, p 447.

(10) Equation only intended to indicate products and not stoichiometry. See text.

Table III. Photolysis of Peresters $RCO_2OC(CH_3)_2R'$ in Pentane and Acetonitrile Solutions at 2537 Å[a]

Perester R	Perester R′	mmol	Solvent[b]	CO_2[c]	RH	R-(–H)	R′H	R′-(–H)	R–R′	Alcohol[d]	Ether[e]	Dmk[f]	ΣR[g]/CO_2
CH_3	CH_3	0.51	P	0.50 (98)	0.37				0	0.33	0.14	t[h]	1.01
CH_3	CH_3	0.49	A	0.45 (92)	0.55				0	0.20	0.08	0.17	
CH_3	CH_2CH_3	0.51	A	0.48 (94)	0.38		0.25	0.01	0.04 0.01[i]	0.01	0.08	0.37	1.00
CH_3	$CH(CH_3)_2$	0.53	A	0.50 (95)	0.38		0.14	0.08	0.08 0.02[j,k]	0.01	0.08	0.37	1.07
CH_3	$CH(CH_3)_2$	0.50	P	0.46 (92)	0.34		0.12	0.08	0.07	0.10	0.07	0.26	1.04
$(CH_3)_2CH$	CH_3	0.51	A	0.47 (92)	0.13	0.13	0.19		0.02 0.02[l,k]	0.26	0.04	0.17	0.77
$(CH_3)_2CH$	CH_3	0.49	P	0.47 (96)	0.14	0.18	t		0	0.41	0.04	t	0.77
$(CH_3)_2CH$	CH_2CH_3	0.51	A	0.46 (90)	0.10	0.10	0.24	0.01	0.05 0.02[l]	0.05	0.04	0.34	0.65
$(CH_3)_2CH$	CH_2CH_3	0.50	P	0.45 (90)	0.13	0.16	0.02	t	t	0.36	0.04	0.04	0.76

[a] Five milliliters of approximately 0.1 *M* solutions of peresters (~0.5 mol) at 30°. All runs in duplicate. Yields expressed as mmoles of product; t = trace found. [b] Number in parentheses is yield of CO_2 based on perester charged. [c] Solvent: P = *n*-pentane, A = acetonitrile. [d] $R'C(CH_3)_2OH$. [e] $R'C(CH_3)_2OR$. [f] Acetone. [g] ΣR includes all products derived from R. [h] Traces ⩽0.01 mmol. [i] R′–R′ = *n*-butane. [j] R′–R′ = 2,3-dimethylbutane. [k] No ethane. [l] R–R = 2,3-dimethylbutane.

Table IV. Stoichiometric Relationships Among Products from the Photolysis of Peresters $RCO_2OC(CH_3)_2R'$ in Decalin[a]

Perester R	Perester R′	[ΣR′-$(CH_3)_2$-CO·][b]/[CO_2]	[R′$(CH_3)_2$-COH]/[R′$(CH_3)_2$-COR]	[R′$(CH_3)_2$-COH]/[R′$(CH_3)_2$-COR + R(–H)]	[ΣR′][c]/[$(CH_3)_2CO$]	[ΣR][d]/[CO_2]	[RH]/[R(–H)]	[R′H]/[R′(–H)	[R′$(CH_3)_2$-COH]/[$(CH_3)_2CO$]
CH_3	CH_3	0.91	1.09	1.09	*e*	0.94			>50
CH_3CH_2	CH_3	0.96	1.42	1.08		1.0	3.5		>50
$(CH_3)_2CH$	CH_3	0.94	3.7	1.08		0.92	0.46		>50
$(CH_3)_3C$	CH_3	0.94	22.5	1.15		0.93	0.18		>50
CH_3	CH_2CH_3	0.96	1.05	1.05	1.0	0.92			5.5
CH_3CH_2	CH_2CH_3	1.0	1.55	1.16	~1	*e*	4.2		7.0
$(CH_3)_2CH$	CH_2CH_3	0.98	3.6	1.28	~1	0.77	0.55		9.0
$(CH_3)_2CH$	CH_2CH_3	0.91	37	1.32	~1	0.84	0.28		12
CH_3	$CH(CH_3)_2$	0.94	0.64	0.64	1.05	0.94		2.2	0.41
CH_3CH_2	$CH(CH_3)_2$	0.88	0.92	0.73	1.13	0.92	9.7	2.3	0.50
$(CH_3)_2CH$	$CH(CH_3)_2$	0.92	3.7	0.92	*e*	*e*	1.45	1.4	1.2
$(CH_3)_3C$	$CH(CH_3)_2$	0.96	27	1.12	1.06	0.73	0.44	2.0	1.7

[a] Taken from data in Tables II and III. [b] Includes $R'(CH_3)_2COH$, $R'(CH_3)_2COR$, and acetone. [c] ΣR′· includes all products derived from R′. [d] ΣR includes all products derived from R. [e] Indeterminate, R = R′.

alkyl or alkoxy radicals with solvent-derived radicals were, in general, not analyzed. The material balance shows that these could not have been formed in significant amounts. However, the material balance of the alkyl (R–) group was generally not as satisfactory as that from the alkoxy group [$R'(CH_3)_2CO$–].

We interpret these results as stemming from an alkyl radical and an alkoxy radical. Such a radical pair may arise directly from the photolysis of the perester or indirectly *via* decarboxylation of an acyloxy precursor (*vide infra*). For purposes of further dis-

$$RCO_2OC(CH_3)_2R' \longrightarrow [R\cdot + CO_2 + \cdot OC(CH_3)_2R'] \quad (3)$$

cussion, we treat the results in terms of the subsequent interactions of the alkyl and alkoxy radical pair within the solvent cage or by diffusion into the bulk solution. The formation of a variety of alkyl radicals (R·)

$$[R\cdot + CO_2 + OC(CH_3)_2R'] \xrightarrow{\text{cage}} CO_2 + [R\cdot\ \cdot OC(CH_3)_2R'], \text{ etc.} \quad (4)$$

$$[R\cdot\ \cdot OC(CH_3)_2R'] \xrightarrow{\text{diffuse}} R\cdot + \cdot OC(CH_3)_2R', \text{ etc.} \quad (5)$$

derived by photolytic scission of the alkyl–carbonyl bond has been demonstrated by esr studies in a large number of examples.[5,6]

Photolysis of a Mixture of Peresters. The sole ethereal products derived from the photolysis of a mixture of *t*-butyl peracetate and *t*-amyl perpropionate in *n*-pentane or decalin solutions were *t*-butyl methyl ether and *t*-amyl ethyl ether. Neither of the crossed ethers, *t*-butyl ethyl ether or *t*-amyl methyl ether, was detected.

Combination and Disproportionation of Alkyl–Alkoxy Radical Pairs. Alkyl–alkoxy radical pairs react by combination (eq 6) or by disproportionation (eq 7).[11]

$$\begin{tikzcd} & ROC(CH_3)_2R' \quad (6) \\ R\cdot + \cdot OC(CH_3)_2R' \arrow[ur, "k_c"] \arrow[dr, "k_d"'] & \\ & R(\text{-}H) + HOC(CH_3)_2R' \quad (7) \end{tikzcd}$$

These bimolecular reactions may occur within a solvent cage (geminate) or in the bulk solution after diffusion from the cage.[12] The photolysis of mixtures of

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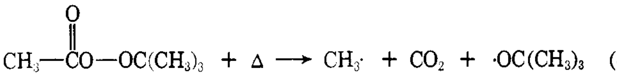
(11) P. Gray, R. Shaw, and J. C. Thynne, *Progr. Reaction Kinetics*, 4, 63 (1968).

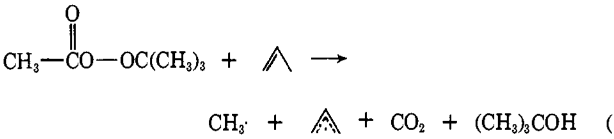
(12) We employ the term cage loosely here and in subsequent discussions. The operational definition is based simply on whether alkyl and alkoxy radicals derived from a given perester molecule combined with radicals from other perester molecules. It is not clear that this concept of a cage reaction is quantitatively equivalent to that based on scavenger studies.[13,14] The latter is difficult to apply quantitatively to these photolyses at 2537 Å due to the lack of suitably transparent scavengers.

peroxides, however, gave no mixed ethers and this suggests that combination and disproportionation of alkyl–alkoxy radical pairs only occur within the solvent cage.[15] The lifetime of the highly reactive *t*-alkoxy radical in bulk solution is short due to facile hydrogen abstraction processes.[16] Encounters between alkoxy radicals and other radical species are thus unlikely outside the solvent cage. These conclusions are qualitatively supported by the examination of the esr spectra taken during photolysis of *t*-butyl and *t*-amyl peracetates. In an inert cyclopropane solution an intense spectrum of only the methyl radical is observed at temperatures less than $-40°$. The steady-state concentration of the *t*-butoxy or *t*-amyloxy radical is too low to observe.[17,18] On the other hand, the same

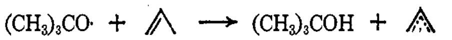


$$CH_3{-}\overset{O}{\overset{\|}{C}}O{-}OC(CH_3)_3 + \Delta \longrightarrow CH_3\cdot + CO_2 + \cdot OC(CH_3)_3 \quad (8)$$

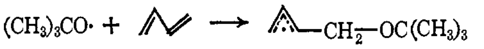
photolysis in the presence of propylene produces simultaneously a spectrum of methyl and allyl radical.[19] The latter is no doubt due to the reaction of those *t*-butoxy radicals which have diffused from the solvent cage and reacted with propylene. In a similar manner, photolysis of *t*-butyl peracetate in dilute solutions of 1,3-butadiene in cyclopropane produced a well-resolved spectrum of the allylic adduct.[20] Alkyl–alkoxy radical pairs from peresters, thus behave differently with variation in solvent than alkyl–alkyl radical pairs from diacyl peroxides observed earlier.[7] A number of the alkyl radicals from diacyl peroxides were shown to undergo collisions outside the solvent cage in solvents of low viscosity. The difference is due to the lower reactivity of alkyl radicals,[21] and hence longer lifetime than their alkoxy counterparts. Esr studies also showed that radicals derived secondarily from solvent (by hydrogen abstraction) were not important species during photolysis of diacyl peroxides.[5,7]



(9)



(10)



(11)

There is a consistent and marked increase in the ratio of alcohol to ether, $R'(CH_3)_2COH:R'(CH_3)_2COR$, in the series: R = methyl < ethyl < isopropyl < *t*-butyl for the homologous *t*-butyl, *t*-amyl, and 2,3-dimethyl-2-butyl peresters (column 3, Table IV). We attribute this trend to an increase in the amount of disproportionation relative to combination between various alkyl–alkoxy radical pairs. By analogy with disproportionation–combination ratios in alkyl–alkyl radical pairs, we expect disproportionation between alkyl and alkoxy radical pairs to increase in the same manner: ethyl < isopropyl < *t*-butyl (methyl is of course excluded).[22] Disproportionation is not, however, the only source of alcohol since it is also formed from *t*-alkoxy radicals by hydrogen transfer from solvent. The contribution from this reaction is expected to be largely independent of R′ (*i.e.*, the total amount of the cage reaction is unaffected by variations in $R'(CH_3)_2CO\cdot$). This is borne out by the almost constant ratio of alcohol to ether plus alkene $[R'(CH_3)_2COH]:[R'(CH_3)_2COR + R(-H)]$, through the three series of peresters including R = methyl, ethyl, isopropyl, and *t*-butyl (column 4, Table IV).[23]

Alkyl radical dimers (R–R, R–R′, and R′–R′) were only minor products from reactions in decalin.[24] The formation of alkenes *via* disproportionation of alkyl radical pairs, therefore, must be negligible. The crossed dimer (R–R′) is most significant with 2,3-dimethyl-2-butyl peresters, and absent with *t*-butyl peresters. It is not clear from an examination of the data (Tables II and III) whether these arise by reactions between R′· (formed by fragmentation of the alkoxy intermediate) and R· within the solvent cage or in the bulk solution.[25]

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[13] *Cf.* P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, **82**, 1760 (1960).

[14] (a) G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950); (b) R. C. Lamb and J. G. Pacifici, *ibid.*, 86, 914 (1964); 84, 2635 (1962); **91**, 5034 (1969); (c) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962); (d) F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961); (e) H. J. Shine, J. A. Waters, and D. M. Hoffman, *ibid.*, **85**, 3613 (1963).

[15] There is a possibility of a duality of mechanisms. Thus, cage combination of alkyl and alkoxy radicals cannot be rigorously distinguished at this juncture from a concerted molecular process. The two mechanisms differ fundamentally in the timing of the bond-breaking processes, and we hope to obtain lower limits for these rates by examining optically active peresters.

[16] (a) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **89**, 4891 (1967); (b) C. Walling and V. P. Kurkov, *ibid.*, **89**, 4895 (1967); (c) P. Gray, R. Shaw, and J. Thynne, *Progr. Reaction Kinetics*, **4**, 68 (1968).

[17] (a) No di-*t*-butyl peroxide was observed in the photolysis of *t*-butyl peresters. (b) The esr spectrum of *t*-butoxy radical has recently been observed by photolysis of neat di-*t*-butyl peroxide.[18]

[18] (a) S. Weiner and G. S. Hammond, *J. Amer. Chem.Soc.*, **91**, 2182 (1969); (b) see, however, M. C. R. Symons, *ibid.*, **91**, 5924 (1969).

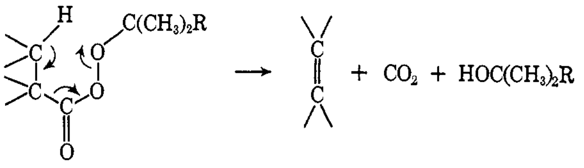
[19] J. K. Kochi and P. J. Krusic, *ibid.*, **90**, 7157 (1968).

[20] Only the *trans* isomer is formed.[19]

[21] (a) K. U. Ingold, "Free Radicals in Solution," I.U.P.A.C. Symposium, Vol. 15, Butterworths, London, 1967, pp 49 ff. (b) Under our experimental conditions products derived from attack on pentane were minor.[7]

[22] In relation but not directly proportional to the number of β-hydrogens available in the alkyl radical: J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 107 (1961).

[23] An alternative explanation which is also consistent with the data is a competition between ether formation *via* alkyl–alkoxy radical combination and alkene formation by a concerted molecular process shown below. The latter reaction has the same stoichiometry as the homolytic



route, and it is difficult to differentiate rigorously between these two alternatives. Evidence which favors the free radical mechanism is the decreased yield of alkene observed on changing the solvent from decalin to pentane or acetonitrile. A molecular process would not be expected to change from decalin to pentane and may even be expected to increase relative to a homolytic process on changing from decalin to the more polar acetonitrile. A radical cage reaction, on the other hand, decreases in importance on changing from decalin to pentane or acetonitrile due to the decrease in solvent viscosity. Reduced yields of alkenes were also observed in thermal decompositions carried out in decalin at 115° consistent with the radical process (*vide infra*).

[24] Yields of symmetrical alkyl dimers, R–R were also curiously minor when photolyses were carried out in *n*-pentane. It was shown earlier[7] that significant amounts of dimers arose from noncage combination of alkyl radicals derived from diacyl peroxides. The magnitude of the cage effects and steady-state concentrations of the radicals are about the same in these two systems.

[25] The formation of propylene from 2,3-dimethyl-2-butyl peresters by a molecular process shown below may be discounted by the complete absence of carboxylic acid among the products. Simpson and Miller[3] found significant amounts of acid (by alkali titration) in the photolysis

Table V. Disproportionation–Combination Ratios for Alkyl–Alkoxy Radical Pairs in Decalin at 30°

Alkyl $R\cdot$	Alkoxy $R'(CH_3)_2CO\cdot$	k_d/k_c $R(-H)/ROC(CH_3)_2R'$	k_d/k_c[a] $R(-H)/R\text{-}R$	k_d/k_c[b] CH_4/RCH_3
$CH_3CH_2\cdot$	CH_3-	0.32	0.14	0.039
$CH_3CH_2\cdot$	CH_3CH_2-	0.33		
$CH_3CH_2\cdot$	$(CH_3)_2CH-$	0.25		
$(CH_3)_2CH\cdot$	CH_3-	2.4	1.2	0.22
$(CH_3)_2CH\cdot$	CH_3CH_2-	1.8		
$(CH_3)_2CH\cdot$	$(CH_3)_2CH-$	2.7		
$(CH_3)_3C\cdot$	CH_3-	19	7.2	0.90
$(CH_3)_3C\cdot$	CH_3CH_2-	27		
$(CH_3)_3C\cdot$	$(CH_3)_2CH-$	23		

[a] Reference 7. [b] Gas phase values for cross-disproportionation of $CH_3\cdot$ and alkyl to cross-combination [J. A. G. Dominguez, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3357 (1962); R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, **67**, 2273 (1963)].

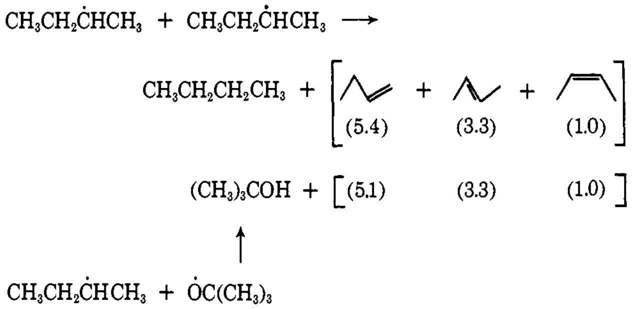
The disproportionation–combination ratios, k_d/k_c, of alkyl–alkoxy radical pairs in decalin are compared with the corresponding ratios for alkyl–alkyl radical pairs[7] in Table V. The latter are represented by self-disproportionation–combination (column 3) and cross-disproportionation–combination (column 4) ratios obtained from study of a pair of alkyl radicals ($R\cdot + R\cdot$) and a methyl radical with an alkyl radical ($CH_3\cdot + R\cdot$), respectively. The tabulated ratios of k_d/k_c are based on the assumption that all of the alkenes [R(–H)] are formed *via* disproportionation of alkyl–alkoxy radical pairs.[26] In each case the values of k_d/k_c between alkyl–alkoxy radical pairs are approximately twice as large as those for self-disproportionation–combination of alkyl–alkyl radical pairs. Further, these ratios increase in parallel in the series: R = ethyl < isopropyl < *t*-butyl (Table VI).[27] The variations in the relative values of k_d/k_c are largely attributed to k_d.[28]

Table VI. Relative Values for Disproportionation–Combination of Alkyl–Alkyl and Alkyl–Alkoxy Radical Pairs[a]

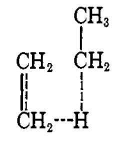
	k_d/k_c			
Alkyl radical $R\cdot$	$R\cdot + R\cdot$	$R\cdot +$ *t*-BuO$\cdot$	$R\cdot + R'O\cdot$[b]	$R\cdot + CH_3\cdot$[c]
$CH_3CH_2\cdot$	1.0	1.0	1.0	1.0
$(CH_3)_2CH\cdot$	8.6	7.5	7.7	5.7
$(CH_3)_3C\cdot$	52	60	77	23

[a] Based on the value for ethyl radical = 1.0. [b] Average from *t*-butoxy, *t*-amyloxy, and 2,3-dimethylbutoxy radicals, see Table V. [c] Gas phase results.

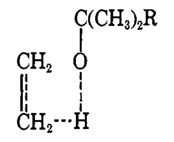
This conclusion is supported by a comparison of intramolecular competition in the disproportionation of the *sec*-butyl radical. Thus, the self-disproportionation of *sec*-butyl radicals[7,29] produces a mixture of butenes of the same composition as that derived from a *sec*-butyl–*t*-butoxy radical pair from the photolysis of *t*-butyl per-2-methylbutyrate. We interpret the parallel



between the behavior of alkyl and alkoxy radicals in the disproportionation process to related transitions states A and B [transition states for ethyl–ethyl disproportionation (A) and ethyl–alkoxy disproportionation (B)]. The latter is somewhat unexpected since alkoxy radicals generally show considerably different selectivities to hydrogen atom transfer reactions than alkyl radicals.[30] This discrepancy can be minimized if bond breaking has not proceeded very far in the transition state of the disproportionation process, a conclusion which is consistent with the large exothermicity of the reaction.[31–33]



A



B

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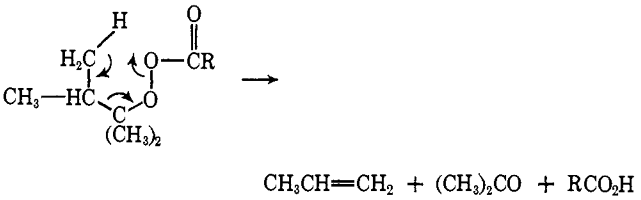
of neat peresters. Their process, however, was complicated by induced decompositions and a number of other routes (unimportant under our conditions) were available for the formation of acids.



(26) The disproportionation between alkyl–alkyl radical pairs complicates this assumption somewhat, especially in the case of 2,3-dimethyl-2-butyl peresters in which alkoxy fragmentation is significant. Consistency in the values of k_d/k_c for the three series of peresters, however, indicates that the problem is minor.

(27) The gas-phase values for the cross disproportionation–combination of methyl and alkyl radicals are difficult to interpret quantitatively, although the trend is the same.

(28) (a) Since we expect the differences of rates of combination of an alkyl radical with another alkyl radical or an alkoxy radical to be nil or small; (b) compare, however, variations in the rates of combination of alkyl radicals: S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 986 (1969); **90**, 1659 (1968); D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).

(29) Similar values have been obtained in the gas phase: J. W. Kraus and J. G. Calvert, *ibid.*, **79**, 5921 (1957); P. J. Boddy and J. C. Robb, *Proc. Roy. Soc.* (London), **A249**, 518, 532, 547 (1959); B. S. Rabinovitch and R. W. Diesch, *J. Chem. Phys.*, **30**, 735 (1959); *cf.* also P. Ausloos, *J. Phys. Chem.*, **65**, 1616 (1961).

(30) C. Walling, ref 21, pp 69 ff.

(31) The difference in activation energies between disproportionation and combination of alkyl radicals is less than 1 kcal/mol (J. A. Kerr and A. F. Trotman-Dickenson, *J.Chem. Soc.*, 1602 (1960); also footnote *b*, Table V). Disproportionation reactions between alkyl–alkyl and alkyl–alkoxy radical pairs are some 50–80 kcal/mol exothermic.

(32) Based on a postulate by G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(33) For a discussion of transition states for disproportionation of alkyl radicals see A. F. Trotman-Dickenson, *Proc. Chem. Soc.* (London), 249 (1964); compare also S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964);

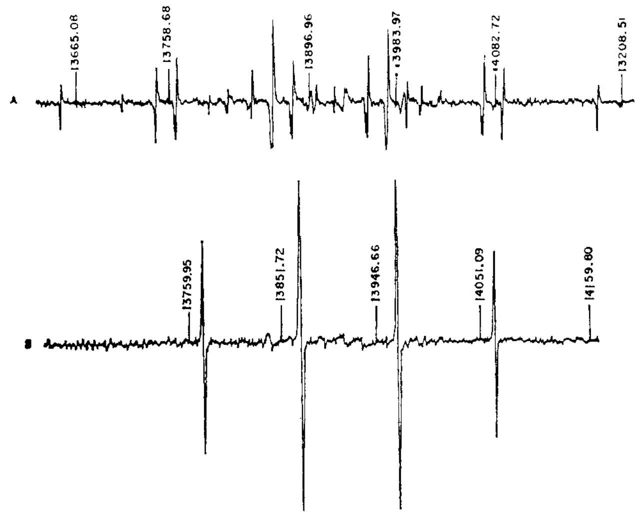


Figure 1. (a) The esr spectrum of ethyl radical from the photolysis of *t*-butyl perpropionate at −90°. (b) The esr spectrum of methyl radical from the photolysis of *t*-amyl peracetate at −90°.

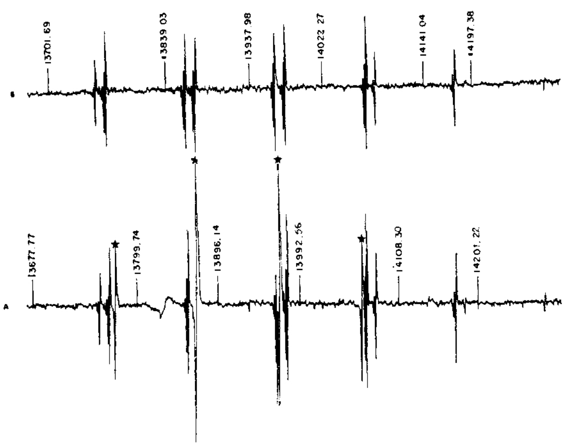


Figure 2. (a) The esr spectrum of methyl (starred) and isopropyl radicals from the photolysis of 2,3-dimethyl-2-butyl peracetate at −90°. (b) The esr spectrum of isopropyl radical from the photolysis of *t*-butyl perisobutyrate.

Fragmentation of Alkoxy Radicals. Product studies show that the fragmentation (eq 12) of the photochemically produced alkoxy radicals increases in importance in the order: R′ = methyl < ethyl < isopropyl (see Table IV, column 9). It also increases on changing the

$$\mathrm{R'C(CH_3)_2O\cdot \longrightarrow R'\cdot + (CH_3)_2CO} \qquad (12)$$

solvent from decalin or pentane to acetonitrile. These results are in qualitative agreement with previous studies on the effect of structure[34] and solvent[35] on the ease of fragmentation of *t*-alkoxy radicals.

Esr studies also show that alkyl radicals formed in steady state from the photolysis of these peresters depend markedly on R′·. Thus, the esr spectrum of only the ethyl radical is observed during photolysis of *t*-butyl perpropionate (Figure 1a) at −115°. The photolysis of the isomeric *t*-amyl peracetate under the same conditions generates only methyl radical in sufficiently high steady-state concentrations to observe the esr spectrum (Figure 1b). In both cases the signal-to-noise ratio increases as the temperature is lowered, and optimum conditions generally call for the lowest temperature obtainable before crystallization commences.[36] It is clear that photolyses of these peresters generate alkyl radicals (R·) by alkyl–carbonyl cleavage, and the fragmentation of *t*-butoxy or *t*-amyloxy radical is minor at these temperatures.

$$\mathrm{CH_3CH_2\overset{\overset{O}{\|}}{C}OOC(CH_3)_3 \longrightarrow CH_3CH_2\cdot + CO_2 + \cdot OC(CH_3)_3} \qquad (13)$$

$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}OOC(CH_3)_2CH_2CH_3 \longrightarrow CH_3\cdot + CO_2 + \cdot OC(CH_3)_2CH_2CH_3} \qquad (14)$$

On the other hand, photolysis of 2,3-dimethyl-2-butyl peracetate under the same conditions generates both the esr spectrum of the isopropyl radical in addition to that of the methyl radical (Figure 2a). The intensity of the esr spectrum of the isopropyl radical relative to the methyl radical decreases as the temperature is lowered, until at −150° only the spectrum of the methyl radical is observed. As expected, only the esr spectrum of the isopropyl radical was recorded during photolysis of the isomeric *t*-butyl perisobutyrate (Figure 2b).

$$\mathrm{CH_3CO_2OC(CH_3)_2CH(CH_3)_2 \longrightarrow CH_3\cdot + CO_2 + (CH_3)_2CO + \cdot CH(CH_3)_2} \qquad (15)$$

$$\mathrm{(CH_3)_2CH\overset{\overset{O}{\|}}{C}OOC(CH_3)_3 \longrightarrow (CH_3)_2CH\cdot + CO_2 + \cdot OC(CH_3)_3} \qquad (16)$$

During the photolysis of *t*-amyl peracetate in cyclopropane at −100° only the esr spectrum of the methyl radical is apparent. Ethyl radicals from the *t*-amyl moiety are not observed until a temperature of −50° is reached. At the other extreme, the relative intensities of the methyl and benzyl radicals from the photolysis of phenyl-*t*-butyl peracetate remained invariant up to the lowest temperatures (−150°) we were able to attain.

$$\mathrm{CH_3CO_2OC(CH_3)_2CH_2Ph \longrightarrow CH_3\cdot + CO_2 + (CH_3)_2CO + \cdot CH_2Ph} \qquad (17)$$

These observations are consistent with two processes leading to R· and R′·, with the activation energy of the latter being higher than that of the former and highly dependent on the structure of R′·. These processes are formulated as[37]

$$\mathrm{RCO_2OC(CH_3)_2R' \longrightarrow R\cdot + CO_2 + \cdot OC(CH_3)_2R'} \qquad (18)$$

$$\mathrm{R'(CH_3)_2CO\cdot \longrightarrow R'\cdot + (CH_3)_2CO} \qquad (19)$$

A. Stefani, *J. Amer. Chem. Soc.*, **90**, 1694 (1968); for pressure dependence see R. C. Neuman, Jr., and J. V. Behar, *Tetrahedron Lett.*, 3281 (1968); *J. Amer. Chem Soc.*, **91**, 6024 (1969); P. S. Dixon, A. P. Stefani, and M. Szwarc, *ibid.*, **85**, 2551 (1963).

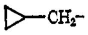
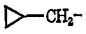
(34) (a) F. D. Greene, M. L. Savitz, F. D. Osterholz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963); (b) C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, **85**, 1593 (1963).

(35) (a) C. Walling and P. J. Wagner, *ibid.*, **85**, 2333 (1963); (b) J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, **30**, 3272 (1965).

(36) Compare also ref 5 and P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **90**, 7155 (1968), in which alkyl radicals were generated by hydrogen atom transfer with *t*-butoxy radicals.

(37) (a) It is unlikely that isopropyl and benzyl radicals are produced from 2,3-dimethyl-2-butyl and 1-phenyl-2-methyl-2-propyl peresters, respectively, in the primary photochemical process by multibond homolysis as in the thermolysis of some peresters[1a] [see also, G. S. Misra and V. R. B. Mathur, *Makromol. Chem.*, **126**, 42 (1969)]. (b) However, the difference in energy between the exciting radiation (∼110

Table VII. Ethers from the Photolysis of Peresters at 30°

Perester $RCO_2OC(CH_3)R'$		Solvent	Ether $ROC(CH_3)_2R'$	Viscosity, cP
CH_3-	$-CH_3$	*n*-Pentane	27	0.21 (30°)[a]
CH_3-	$-CH_3$	Decalin	44	1.55 (37°)[b]
CH_3-	$-CH_3$	Decalin (115°)[e]	17	0.59 (115°)[b]
CH_3-	$-CH_3$	Mineral oil (Nujol)	75	79.9 (45°)[c]
CH_3-	$-CH_3$	Acetonitrile	18	0.38 (20°)[d]
	$-CH_3$	Decalin	43	1.55[b]
	$-CH_3$	Mineral oil	75	79.9[c]
CH_3-	$-CH_2CH_3$	Decalin	43	1.55[b]
CH_3-	$-CH_2CH_3$	Acetonitrile	17	0.38[d]
CH_3-	$-CH(CH_3)_2$	*n*-Pentane	15	0.21[a]
CH_3-	$-CH(CH_3)_2$	Decalin	29	1.55[b]
CH_3-	$-CH(CH_3)_2$	Acetonitrile	16	0.38[d]

[a] G. W. C. Kaye and T. H. Laby, "Table of Physical and Chemical Constants," Longmans, London, 1966, p 36. [b] D. H. Hogenboom, W. Webb, and J. A. Dixon, *J. Chem. Phys.*, **46**, 2586 (1967). [c] Reference 40. [d] A.-L. Vierk, *Z. Anorg. Chem.*, **261**, 283 (1956). [e] Thermal decomposition.

We judge from the high quantum yield for carbon dioxide formation that the formation of R· is closely associated with the primary photochemical process (*vide infra*). Other studies have shown that the activation energy and the rate of cleavage of alkoxy radicals are highly dependent on the structure of R′·. For example, at 40° *t*-amyloxy radical fragments to ethyl radical and acetone at least 30 times more slowly than the 2,3-dimethyl-2-butoxy radical produces isopropyl radical.[34b] This difference in the rates of fragmentation of the two alkoxy radicals increases to greater than 400 at less than −100° due to an approximately 2 kcal/mol higher activation energy. The activation energy for fragmentation of the *t*-butoxy radical is the highest in this series (~11 kcal/mol), and the rate is 300 times slower than that of *t*-amyloxy radical at 25°.[38] The metastability of the benzyldimethylmethoxy radical[34b] is also consistent with the esr results. The rather selective fragmentation of these photochemically generated alkoxy radicals indicates that they do not exist for prolonged periods in unusually high vibrational states in contrast to their counterparts generated in the gas phase.[39]

Cage Reactions of Alkyl–Alkoxy Radical Pairs. Since mixtures of peresters on photolysis only afford ethers derived from the parent perester and none from mixed combinations, we conclude that ether formation occurs exclusively by cage recombination of alkyl–alkoxy radical pairs.[12,40] Hence, the photolysis of *t*-butyl peracetate (in which disproportionation to alkene and alcohol is precluded) should afford *t*-butyl methyl ether as the sole cage product. The latter is supported by the absence of acetone (from the fragmentation of the *t*-butoxy radical) and the good accounting of all the *t*-butyl moiety as *t*-butyl alcohol and *t*-butyl methyl ether.

The yields of *t*-butyl methyl ether obtained by photolysis of *t*-butyl peracetate in various solvents are listed in Table VII together with approximate values for the viscosity of the solvent. Approximately the same yields of ethers are obtained from *t*-butyl percyclopropylacetate and *t*-amyl peracetate under similar conditions.[41] However, the photolysis of 2,3-dimethyl-2-butyl peracetate produces significantly diminished yields of 2,3-dimethyl-2-butyl methyl ether due undoubtedly to the ready fragmentation of the 2,3-dimethyl-2-butoxy radical. The lower yields of *t*-butyl methyl ether in acetonitrile compared to pentane can also be attributed to the enhanced rate of fragmentation of *t*-butoxy radical in the more polar solvent.[35,42]

The yield of *t*-butyl methyl ether from the photolysis of *t*-butyl peracetate and other peresters listed in Table VII can be employed as a crude measure of the cage reactions of alkyl–alkoxy radical pairs.[43] The tabu-

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kcal/mol) and that required for homolysis of the peroxy linkage (~40 kcal/mol) is sufficient to leave both the acyloxy and alkoxy fragments in upper vibrational states. Decarboxylation of the acyloxy fragment may proceed from such excited states, although the reaction itself is exothermic by at least 15 kcal/mol.

(38) J. K. Kochi, *J. Amer. Chem. Soc.*, **84**, 1193 (1962).

(39) The absence of significant fragmentation of the *t*-butoxy radicals from *t*-butyl peresters beyond that observed in thermolyses indicates that the photolysis is rather selective. Alkoxy radicals are probably formed close to a ground vibrational state [*cf.* "excited alkoxy radicals" G. R. McMillan, *ibid.*, 83, 3018 (1961); *Oxid. Combust. Rev.*, 1, 84 (1967), and P. Svejda and D. H. Volman, *J. Phys. Chem.*, 73, 4417 (1969)].

(40) The results up to this point do not eliminate the possibility that the ethers arise by a concerted mechanism in which a molecule of carbon dioxide is extruded directly from the perester during the photoactivation process.[15] This nonradical mechanism appears unlikely since preliminary stereochemical studies show that the *t*-butyl peresters of *syn*- and *anti*-7-carboxynorbornene afford the same mixture of *syn*- and *anti*-*t*-butoxynorbornene on photolysis [P. Bakuzis, unpublished results].

(41) Since the fragmentation of *t*-amyloxy radical and the disproportionation of cyclopropylmethyl radical [*cf.* isobutyl radical, D. H. Slater, S. S. Collier, and J. G. Calvert, *J. Amer. Chem. Soc.*, **90**, 268 (1968)] are minor.

(42) No evidence for esters derived by the (cage) combination of acyloxy radicals $RCO_2\cdot$ with alkyl radicals $R'\cdot$ formed from the fragmentation of alkoxy radicals could be found, *e.g.*, no isopropyl acetate

$$RCO_2OC(CH_3)_2R' \longrightarrow RCO_2R' + OC(CH_3)_2$$

from 2,3-dimethyl-2-butyl peracetate. This is consistent with the much higher rate of decarboxylation of acetoxy radicals (if they are intermediates) compared to the fragmentation of alkoxy radicals. Significant amounts of mixed alkyl dimers (R–R′) were obtained only from the photolysis of 2,3-dimethyl-2-butyl peresters.

(43) A number of factors are involved in the efficiency of cage encounters between radical pairs, among which are: (a) the rate of diffusion of the radicals,[44a] (b) the geometry[44b] and spin multiplicity[44c] of the radical pair as first formed, (c) the presence of a third product in the cage, (d) the rate of reaction between the radical and solvent, and (e) the specific rate constant for combination of the two radicals in question. The importance of each of these factors in determining the efficiency of the cage process is difficult to assess quantitatively at this juncture. Qualitatively, cage reactions of radical pairs from azo compounds which produce one intervening nitrogen molecule are more efficient than those from peroxyoxalates or diacyl peroxides which generate two molecules of carbon dioxide.[44d] The cage process between two alkoxy radicals is less efficient than those between alkyl radicals[7,44c] due probably to the slower rate of combination and the higher reactivity toward the solvent cage of alkoxy radicals compared to alkyl radicals.

(44) (a) O. Dobis, J. M. Pearson, and M. Szwarc, *J. Amer. Chem. Soc.*,

Table VIII. Cage Reactions of Alkyl–Alkoxy Radical Pairs in Thermal and Photochemical Decompositions of Peresters

Radical pair		Solvent	Viscosity, cP	Temp, °C	Cage, %	Method[a]	Ref
$(CH_3)_3CO\cdot$	$\cdot CH_2Ph$	Toluene	0.27[b]	95	23	Δ (ether)	*c*
				95	32	Δ (scav)	*c*
$(CH_3)_3CO\cdot$	$\cdot C(CH_3)_2Ph$	Benzene	0.39	60	30	Δ (scav)	*d*
$(CH_3)_3CO\cdot$	$\cdot C(CH_3)_2Ph$	Dodecane	0.94	50	42	Δ (scav)	*d*
$(CH_3)_3CO\cdot$	$\cdot C(CH_3)_2Ph$	Drakeol	24	60	83	Δ (scav)	*d*
$(CH_3)_3CO\cdot$	$\cdot CHPh_2$	Toluene	0.46	40	31	Δ (ether)	*e*
			0.38	60	22	Δ (ether)	*e*
$(CH_3)_3CO\cdot$	$\cdot CPh_3$	Cumene	0.63	26	11	Δ (scav)	*f*
$(CH_3)_3CO\cdot$	· 	Cumene	0.41	80	30	Δ (ether)	*g*
$(CH_3)_3CO\cdot$	$\cdot CH_3$	Pentane	0.21	30	27	*hν* (ether)	This
$(CH_3)_3CO\cdot$	$\cdot CH_3$	Decalin	1.5	30	44	*hν* (ether)	work
$(CH_3)_3CO\cdot$	$\cdot CH_3$	Nujol	80	30	75	*hν* (ether)	This
$(CH_3)_3CO\cdot$	$\cdot CH_3$	Decalin	0.59	115	17	Δ (ether)	work

[a] Δ = thermal, *hν* = photochemical (2537 Å) production of radicals. Cage effect determined by yield (ether and alkene) or (scavenging) with galvinoxyl, oxygen, or iodine. [b] Footnote *a*, Table VII. [c] Reference 13. [d] Reference 46. [e] P. D. Bartlett and L. B. Gortler, *J. Amer. Chem. Soc.*, **85**, 1864 (1963). [f] J. P. Lorand and P. D. Bartlett, *ibid.*, **88**, 3294 (1966). [g] R. C. Neuman, Jr., and J. V. Behar, *Tetrahedron Lett.*, 3281 (1968).

Table IX. Photolysis of Cyclopropylmethyl, Allylcarbinyl, and Cyclobutyl Peresters at 2537 Å and 30° in Decalin[a]

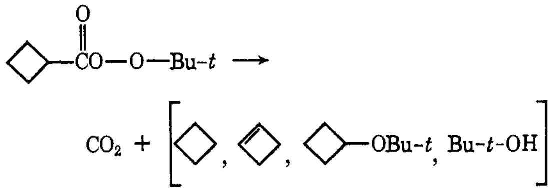
Perester $RC(=O)OOC(CH_3)_3$	Products: CO_2	RH	R(–H)[b]	$(CH_3)_3COH$	$(CH_3)_3COR$	$\Sigma(CH_3)_3CO$[c]/CO_2	ΣR[d]/CO_2
 (0.49)	0.44	 (0.11)[e]	 (t)	0.27	0.16[f]	0.98	0.62
 (0.46)	0.42	 (0.08)	 (0.10)	(0.30)	0.11[g]	0.98	0.69
 (0.51)	0.46	 (0.10)[e]	 (t)	(0.22)	0.17[h] 0.025[i,j]	0.90	0.65
 (0.47)[k]	0.47	 (0.10)	 (t)	(0.18)[l]	0.07[h] 0.01[i,j]	0.77	0.45

[a] Five milliliters of ~0.1 *M* solution photolyzed in duplicate. All yields in millimoles. [b] 1,3-Butadiene not stable to reaction conditions; yields indeterminant; t = traces found. [c] $\Sigma(CH_3)_3CO$ sum of all products derived from *t*-butoxy group. [d] ΣR includes all products from R. [e] No methylcyclopropane or cyclobutane found. [f] *t*-Butyl allylcarbinyl ether, no cyclobutyl or cyclopropylmethyl isomers found. [g] Cyclobutyl *t*-butyl ether, no allylmethyl, allylcarbinyl, or cyclopropylmethyl ethers found. [h] Cyclopropylmethyl *t*-butyl ether. [i] Allylcarbinyl *t*-butyl ether. [j] No cyclobutyl *t*-butyl ether. [k] Acetonitrile solvent. [l] Acetone (0.18 mmol) also present.

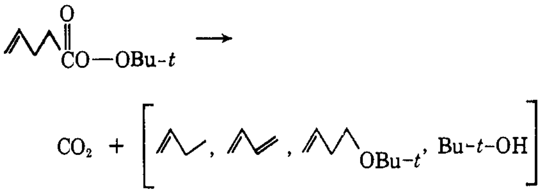
lation in Table VII indicates that the cage reactions of alkyl–alkoxy pairs from peresters are almost as efficient as those involving alkyl–alkyl radical pairs from diacyl peroxides (see ref 7). The increase in cage reactions expected from peresters by removing one molecule of carbon dioxide from the cage has apparently been offset by the facile attack of alkoxy radical on the solvent cage.[45]

The efficiency of the cage reactions may also be influenced by the energy content (translational and vibrational) as well as the spin multiplicity of the alkyl–alkoxy radical pair produced by the photochemical process. Comparisons of the cage processes from the thermal[46] (*vide infra*) and photochemical production of alkyl–alkoxy radical pairs are listed in Table VIII. Since reactions were not carried out or measured by the same methods, quantitative comparisons are not yet justified.[47] It is clear, however, that the viscosity of the solvent is a more important factor than the method of production of radicals in determining their cage interaction.

Rates of Combination of Alkyl and Alkoxy Radicals. The Photolysis of Cyclopropylacetyl, Allylacetyl, and Cyclobutanecarbonyl Peresters. The subject peresters were examined in order to explore the possibility of free radical rearrangements in the homoallylic system.[48] Allylcarbinyl and cyclobutyl peresters gave only products derived from the allylcarbinyl and cyclobutyl radicals, respectively, and no isomeric products were found (Table IX).



(20)



(21)

90, 278 (1968); (b) H. P. Waits and G. S. Hammond, *ibid.*, **86**, 1911 (1964); (c) P. D. Bartlett and J. M. McBride, ref 21, pp 89 ff; S. F. Nelson and P. D. Bartlett, *J. Amer. Chem. Soc.*, 88, 143 (1966); (d) H. Kiefer and T. G. Traylor, *ibid.*, **89**, 6667 (1967); *cf.* also T. Koenig and M. Deinzer, *ibid.*, **90**, 7014 (1968), for nitrogen in the cage with an acyloxy–alkoxy radical pair; (e) K. Chakravorty, J. M. Pearson, and M. Szwarc, *ibid.*, **90**, 283 (1968); L. Herk, M. Feld, and M. Szwarc, *ibid.*, 83, 2998 (1961); J. Smid and M. Szwarc, *ibid.*, 78, 3322 (1956).

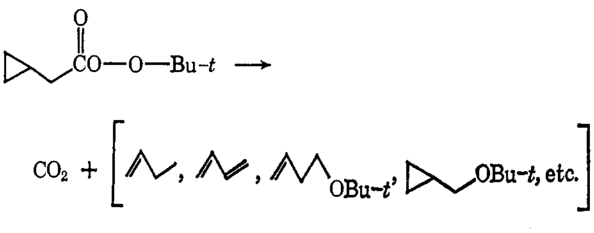
(45) (a) Assuming the rate constants for combination are the same.[28] (b) See also ref 16 and 18.

(46) F. E. Herkes, J. Friedman, and P. D. Bartlett, *Intern. J. Chem. Kinetics*, **1**, 193 (1969).

(47) Different sizes of the alkyl radicals will also have an influence on diffusion rates[50] of radicals and the results are not all comparable. For example, compare $CH_3\cdot$ with the higher homologs in Table VIII.

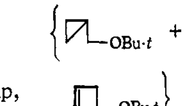
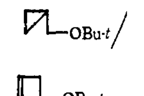
(48) *Cf.* J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 1877 (1968); L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 6556 (1967).

t-Butyl percyclopropylacetate afforded mostly products containing the allylcarbinyl group, the significant exception being the formation of cyclopropylmethyl *t*-butyl ether in addition to allylcarbinyl *t*-butyl ether. The ratio of these two isomeric ethers remained relatively invariant in a variety of solvents. Under the same conditions the combined yields of the ethers varied considerably with changes in the viscosity of the solvent (Table X). Rearrangement did not occur prior to decarboxylation since the perester recovered after photolysis was carried to varying degrees of completion showed no evidence of rearrangement.[49]

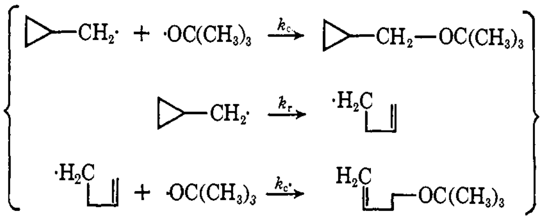


(22)

Table X. Effect of Solvent on the Formation of Ethers from the Photolysis of *t*-Butyl Percyclopropylacetate at 2537 Å

Solvent	Temp, °C	, %	, %
n-Hexane	30	22	5.5
n-Dodecane	30		6.7
n-Hexadecane	30		6.8
Decalin	30	44	6.8
Octane	30		6.1
Mineral oil	30	75	5.9
Acetonitrile	30	17	6.0
n-Butane	−10		~10
Isobutane	−10		~10
Decalin	−10		7.5

The relatively high yields of cyclopropylmethyl *t*-butyl ether from the photolysis of *t*-butyl percyclopropylacetate can be attributed to the cage combination of *t*-butoxy radical B with cyclopropylmethyl radical C (eq 23) in competition with the facile rearrangement of C to allylcarbinyl radical A (eq 24).[48] The cage processes can be represented by reactions 23–25.

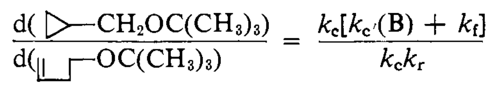


(23)
(24)
(25)

The steady-state concentration of allylcarbinyl radicals is given by eq 26 where k_f is the rate of diffusion

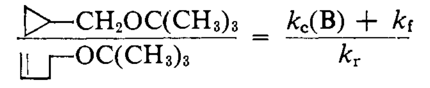
$$\frac{dA}{dt} = k_r(C) - k_{c'}(A)(B) - k_f(A) = 0 \qquad (26)$$

of A out of the cage. The relative rates of formation of cyclopropylmethyl and allylcarbinyl *t*-butyl ethers are then given by eqation 27. Integration leads to



(27)

expression 28 if k_c and k_c' are equated. Since the



(28)

relative yields of cyclopropylmethyl and allylcarbinyl ethers are invariant over a large range of solvent viscosities (Table X) we conclude that $k_c(B) \gg k_f$.[44d,50] Using an average value of 6 for this ratio of ethers,[51] it follows that $6k_r = k_c(B)$, or the rate of combination of alkyl and alkoxy radicals is six times faster than the rate of rearrangement of cyclopropylmethyl radical. If we assume[52] that k_r is 10^8 sec^{-1} then the rate of combination of the radial pair is approximately 10^9 sec^{-1}. The latter value compares with a second-order rate constant ($2k_c$) of 2×10^8 M^{-1} sec^{-1} for the combination of two *t*-butoxy radicals[16,18] and 10^9 and 4×10^9 M^{-1} sec^{-1} for the bimolecular reactions of *n*-pentyl and benzyl radicals, respectively.[28,53]

The Thermal Decomposition of Peresters. A few of the representative peresters were thermally decomposed in decalin at 115° (see Experimental Section, Table XII) for comparison with the photochemical reaction carried out at 30°. Essentially the same products were formed, but the yields of products in which the alkoxy group was intact [$R'(CH_3)_2COR$ and $R'(CH_3)_2COH$] were diminished and those derived from the fragmentation of the alkoxy group [R′H, R′(-H) and acetone] were enhanced. The thermal decomposition of these peresters in acetic acid, however, was complicated by a competing heterolytic process. The latter was most severe with the 2,3-dimethyl-2-butyl peresters judging by the production of isopropyl acetate and alcohol.[2,54]

Comments on the Primary Photochemical Process. The homolysis of peresters can occur by at least three routes

$$RCO_2OC(CH_3)_2R' \longrightarrow RCO_2\cdot + \cdot OC(CH_3)_2R' \qquad (29)$$

$$RCO_2OC(CH_3)_2R' \longrightarrow R\cdot + \cdot CO_2OC(CH_3)_2R' \qquad (30)$$

$$RCO_2OC(CH_3)_2R' \longrightarrow R\cdot + CO_2 + \cdot OC(CH_3)_2R' \qquad (31)$$

The first homolysis (eq 29) is that usually encountered in thermolysis and the second (eq 30) is analogous to a Norrish type I cleavage of ketones. The quantum yield of the latter,[55] however, is significantly less than we observe for peresters. A multibond cleavage

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(49) (a) Under the same condition methyl cyclopropylacetate underwent 4% rearrangement to methyl allylacetate. (b) However, the primary cage recombination of cyclopropylmethyl radical and *t*-butylperoxycarbonyl radical may preclude rearrangement.

(50) (a) R. M. Noyes, *Progr. Reaction Kinetics*, 1, 129 (1961); (b) W. Braun, L. Rajenbach, and F. R. Eirich, *J. Phys. Chem.*, 66, 1591 (1962); (c) T. Koenig, *J. Amer. Chem. Soc.*, 91, 2558 (1969).

(51) (a) This assumes negligible disproportionation between allylcarbinyl-*t*-butoxy radical pairs. (b) Deliberate addition of 1,3-butadiene did not affect this ratio and indicated allylcarbinyl *t*-butyl ether did not arise from addition of *t*-butoxy radical to 1,3-butadiene. (c) See also J. C. Martin and J. W. Timberlake, *J. Amer. Chem. Soc.*, 92, 978 (1970).

(52) Estimated from the value for the isocholesteryl → cholesteryl rearrangement. See D. J. Carlsson and K. U. Ingold, *ibid.*, 90, 7047 (1968).

(53) R. D. Burkhart, *ibid.*, 90, 273 (1968); *J. Phys. Chem.*, 73, 2703 (1969).

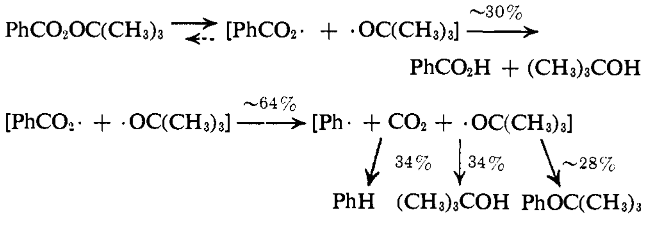
(54) *Cf.* R. Criegee and R. Kaspar, *Ann.*, 560, 127 (1948); R. A. Sheldon and J. K. Kochi, *J. Org. Chem.*, 35, 1223 (1970).

(55) See C. H. Nicols and J. G. Calvert for the effect of structure on Norrish type I and II cleavages (*J. Amer. Chem. Soc.*, 89, 1790 (1967)).

Figure 3. The esr spectrum of cyclopropyl radical from the photolysis of *t*-butyl percyclopropanecarboxylate at −100°. The proton nmr field markers are in kilohertz. Note broad-line absorption at *ca.* $g = 2.00$.

presented as the third alternative (eq 31) appears to be unfavored from an energetic point of view since the energy provided by 2537-Å irradiation (∼110 kcal/mol) is more than sufficient to cause oxygen–oxygen homolysis (∼40 kcal/mol) without added driving force provided by a concerted decomposition.

The photolysis of *t*-butyl perbenzoate in decalin, however, does produce benzoic acid (30%) in addition to phenyl *t*-butyl ether (28%), benzene (34%), *t*-butyl alcohol (68%), and carbon dioxide (64%). The results are best interpreted as a one-bond homolysis followed by further reactions of benzoyloxy and *t*-butoxy radicals. Decarboxylation of benzoyloxy radicals proceeds more slowly than its aliphatic counterparts,[56] and diffusion from the solvent cage would lead to benzoic acid. The lower quantum yields (for carbon dioxide formation) obtained from the photolysis of *t*-butyl perbenzoate could indicate primary recombination of the benzoyloxy and *t*-butoxy fragments.[57b]



$$\mathrm{PhCO_2OC(CH_3)_3} \rightleftarrows [\mathrm{PhCO_2\cdot} + \cdot\mathrm{OC(CH_3)_3}] \xrightarrow{\sim 30\%} \mathrm{PhCO_2H} + \mathrm{(CH_3)_3COH}$$

$$[\mathrm{PhCO_2\cdot} + \cdot\mathrm{OC(CH_3)_3}] \xrightarrow{\sim 64\%} \begin{array}{ccccc} [\mathrm{Ph\cdot} & + & \mathrm{CO_2} + & \cdot\mathrm{OC(CH_3)_3}] & \\ \downarrow 34\% & & \downarrow 34\% & \searrow \sim 28\% & \\ \mathrm{PhH} & & \mathrm{(CH_3)_3COH} & \mathrm{PhOC(CH_3)_3} & \end{array}$$

We favor tentatively a one-bond homolysis of the aliphatic peresters (eq 29).[57a] Within experimental error the quantum yield is one and indicates that primary recombination is not appreciable. Furthermore, the yield is independent of the viscosity of the solvent[58] and the structure of the perester. No carboxylic acid or ester is detected among the products even in the photolysis of *t*-butyl percyclopropanecarboxylate. The cyclopropanecarboxy radical is expected to decarboxylate slower than other acyloxy analogs.[59] A well-resolved esr spectrum of cyclopropyl radical shown in Figure 3 can be obtained from the photolysis of *t*-butyl cyclopropanecarboxylate even at −100°. The fragmentation of acyloxy radicals has been estimated to proceed with a rate of 1.6×10^9 sec^{-1} at 60°.[50b] This rate is probably not significantly less at lower temperatures since the decarboxylation is exothermic ($\Delta H \approx -15$ kcal/mol).[60] Thus, if an acyloxy radical is a precursor, its lifetime is short ($<10^{-7}$ sec). Other chemical processes which may trap it also do not intervene since we see no evidence of its presence among products.

Experimental Section

***t*-Butyl hydroperoxide** (Lucidol Corp., 90%) was vacuum distilled and was 99% pure by iodometric titration. ***t*-Amyl hydroperoxide** was prepared from *t*-amyl alcohol and hydrogen peroxide by the Milas[61a] procedure. **2,3-Dimethyl-2-butanol** was prepared from isopropylmagnesium bromide and acetone and had bp 115–116° (lit.[61b] 117–122°). **2,3-Dimethyl-2-butyl hydroperoxide** was prepared by the method of Criegee[62] and had bp 37° (3 mm). **α,α-Dimethylphenethyl hydroperoxide** was prepared from α,α-dimethylphenethyl alcohol (Givaudan Co.) and hydrogen peroxide, mp 45–46° (lit.[63] 38–41°). ***t*-Butyl peracetate** (Lucidol Corp.) was vacuum distilled and was 99% pure by iodometric titration. **Di-*t*-butyl ether** was prepared from *t*-butyl bromide and silver carbonate and had bp 108–109° (lit.[64] 108–109°). ***t*-Amyl methyl ether** was prepared from *t*-amyl alcohol and methanol with a catalytic amount of concentrated sulfuric acid and had bp 84–85° (lit.[65] 86–87°). ***t*-Amyl ethyl ether** was prepared from *t*-amyl alcohol and ethyl alcohol and had bp 100–102° (lit.[65] 101–102°). ***t*-Amyl isopropyl ether** was prepared from *t*-amyl alcohol and isopropyl alcohol and had bp 114–116° (lit.[65] 114–115°). **Methyl 2,3-dimethyl-2-butyl ether** was prepared from sodium 2,3-dimethyl-2-butoxide and methyl iodide and had bp 110–111°. **Ethyl 2,3-dimethyl-2-butyl ether** and **isopropyl 2,3-dimethyl-2-butyl ether** were prepared in solution by reaction of the respective alcohols in the presence of concentrated sulfuric acid but yields were so poor that isolation was unsuccessful. ***t*-Butyl 3-butenyl ether** was prepared by stirring 3-buten-1-ol (3.6 g) and *t*-butyl alcohol (5.5 g) at 60° for 12 hr. The solution was diluted with pentane and washed continually with water until no *t*-butyl alcohol remained. The pentane was removed at atmospheric pressure and the residue distilled to give *t*-butyl 3-butenyl ether: 0.7 g (10%); bp 109–110°; nmr τ 4.8–6.1 (3 H, multiplet), 3.33 (2 H, triplet), 2.20 (2 H, multiplet), 1.14 (9 H, singlet). *Anal.* Calcd for $C_8H_{16}O$: C, 75.00; H, 12.50. Found: C, 74.79; H, 12.56. Attempted preparation of **cyclopropylcarbinyl *t*-butyl ether** and **cyclobutyl *t*-butyl ether** by reaction of the corresponding alcohols in the presence of concentrated sulfuric acid gave mixtures of the three isomeric *t*-butyl ethers, cyclopropylcarbinyl, 3-butenyl, and cyclobutyl. Sodium *t*-butoxide and cyclobutyl *p*-toluenesulfonate in *t*-butyl alcohol gave a small amount of cyclobutyl *t*-butyl ether which was not isolable. The product, presumed to be cyclobutyl *t*-butyl ether, obtained in the above reactions, had a retention time identical with the product obtained in the photolysis of *t*-butyl percyclobutanecarboxylate. ***t*-Butyl allyl ether** was obtained in 22% yield by reaction of *t*-butyl alcohol with allyl alcohol in the presence of concentrated sulfuric acid and had bp 96–98° (lit.[66] 99–100°).

Cyclopropylcarbinyl *t*-butyl ether was prepared in 65% yield from *t*-butyl allyl ether, methylene iodide, and zinc–copper couple using the LeGoff procedure[67] and had bp 120–121°: nmr 3.13 (2 H, doublet), 1.13 (9 H, singlet), 0–1.0 (5 H, multiplet). *Anal.* Calcd for $C_8H_{16}O$: C, 75.00; H, 12.50. Found: C, 74.86; H, 12.37.

Methyl cyclopropylacetate was prepared from cyclopropylacetic acid and methanol in the presence of a catalytic amount of concentrated sulfuric acid and had bp 134–135° (lit. 128–132° (748 mm)). Similarly, methyl cyclobutanecarboxylate and methyl allylacetate were prepared from cyclobutanecarboxylic acid and allylacetic acid and had bp 143–135° (lit. 136–136.5°) and 127–129°, respectively.

Peresters were prepared either by the pyridine acylation method[1a] or by the carbonyldiimidazole method (see Table XI).[63] All the

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[56] D. F. DeTar, *J. Amer. Chem. Soc.*, 89, 4058 (1967).

[57] (a) However, results from the photolysis of *t*-butyl perbenzoate are not necessarily adaptable to aliphatic peresters, since it is not clear that the primary photophysical process involves only the peroxycarbonyl function without also involving the phenyl chromophore. (b) Oxygen scrambling experiments would help to support such a possibility. *Cf.* J. C. Martin and J. H. Hargis, *ibid.*, 91, 5399 (1969).

[58] For a discussion of multibond cleavage and the viscosity of the medium *cf.* W. A. Pryor and K. Smith, *ibid.*, 89, 1741 (1967).

[59] G. Greig and J. C. J. Thynne, *Trans. Faraday Soc.*, 63, 1369, 2197 (1967).

[60] (a) M. Szwarc, "Peroxide Reaction Mechanism," J. O. Edwards, Ed., Interscience Publishers, New York, N. Y., 1962, p 153 ff. (b) J. C. Martin and S. A. Dombchik, "Oxidation of Organic Compounds," Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 269.

[61] (a) N. Milas and D. Surgenor, *J. Amer. Chem. Soc.*, 68, 205 (1946); (b) M. Delacre, *Chem. Zent.*, 77, 1234 (1906).

[62] R. Criegee and H. Dietrich, *Ann.*, 135 (1948).

[63] J. Kochi and F. Rust, *J. Amer. Chem. Soc.*, 83, 2007 (1961); 86, 5264 (1964).

[64] E. Smutny and A. Bondi, *J. Phys. Chem.*, 65, 546 (1961).

[65] T. Evans and K. Edlund, *Ind. Eng. Chem.*, 28, 1186 (1936).

[66] E. Talley, A. Hunter, and E. Yanovsky, *J. Amer. Chem. Soc.*, 73, 3528 (1951).

[67] E. LeGoff, *J. Org. Chem.*, 29, 2048 (1964).

Table XI. Preparation and Properties of Peresters $RCO_2OC(CH_3)_2R'$

R′	R	Method of preparation[a]	% yield	Bp, °C	Empirical formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
Methyl	Ethyl	*a*	83	34–35 (2.8 mm)	$C_7H_{14}O_3$				
Methyl	Isopropyl	*a*	87	36 (2.2 mm)	$C_8H_{16}O_3$				
Methyl	*t*-Butyl	*a*	78	28–30 (1.0 mm)	$C_9H_{18}O_3$				
Methyl	3-Butenyl	*b*	70	43–44 (0.7 mm)	$C_9H_{16}O_3$	62.8	9.3	62.49	9.28
Methyl	Cyclobutyl	*b*	93	50–51 (0.9 mm)	$C_9H_{16}O_3$	62.8	9.3	61.85	9.45
Methyl	Cyclopropyl carbinyl	*b*	85	49–50 (1.0 mm)	$C_9H_{16}O_3$	62.8	9.3	62.60	9.23
Methyl	Cyclopropyl	*b*	73	42–43 (1.0 mm)	$C_8H_{14}O_3$	60.8	8.9	60.43	9.04
Ethyl	Methyl	*a*	71	39 (3 mm)	$C_7H_{14}O_3$				
Ethyl	Ethyl	*a*	83	46 (2.5 mm)	$C_8H_{16}O_3$	60.0	10.0	59.71	10.21
Ethyl	Isopropyl	*a*	70	45 (1.3 mm)	$C_9H_{18}O_3$	62.1	10.3	61.97	10.26
Ethyl	*t*-Butyl	*a*	73	50 (1.7 mm)	$C_{10}H_{20}O_3$	63.8	10.6	63.64	10.66
Isopropyl	Methyl	*a*	65	40 (1.7 mm)	$C_8H_{16}O_3$	60.0	10.0	59.85	10.05
Isopropyl	Ethyl	*a*	78	50 (1.7 mm)	$C_9H_{18}O_3$	62.1	10.3	62.2	10.35
Isopropyl	Isopropyl	*a*	88	56–58 (1.8 mm)	$C_{10}H_{20}O_3$	63.8	10.6	63.45	10.93
Isopropyl	*t*-Butyl	*a*	30	51–52 (1.0 mm)	$C_{11}H_{22}O_3$	65.3	10.9	65.06	10.96
Benzyl	Methyl	*a*	74						

[a] Method a, see ref 1a. [b] Method b, see ref 68.

Table XII. Thermal Decomposition of Some Peresters $RCO_2OC(CH_3)_2R'$ in Decalin and Acetic Acid[a]

Perester					Products							
R	R′	Concn, *M*	Solvent[b]	Time[c]	CO_2	RH	R(–H)	R′H	R′(–H)	$(CH_3)_2$-CO	$R'(CH_3)_2$-COH	$R'(CH_3)_2$OR
CH_3	CH_3	0.54	d	360	0.48	0.38	t			0.02	0.38	0.08
CH_3	CH_2CH_3	0.50	d	360	0.47	0.35		0.16		0.17	0.21	0.08
CH_3	$CH(CH_3)_2$	0.50	d	360	0.46	0.38	0	0.32	0.01	0.34	0.04	0.06^{d}
CH_3	$CH(CH_3)_2$	0.50	a	480	t	t	t	0.03		0.36	0.01	0^{a}
CH_3CH_2	$CH(CH_3)_2$	0.50	a	480	t	t	0	t	0.02	0.34	0.01	0^{d}
$(CH_3)_2CH$	CH_3	0.50	d	60	0.45	0.21	0.09	t		0.01	0.37	0.07
$(CH_3)_2CH$	CH_2CH_3	0.51	d	60	0.47	0.22	0.09	0.16		0.16	0.26	0.06
$(CH_3)_2CH$	$CH(CH_3)_2$	0.50	d	60	0.49	0.45	0.11			0.27	0.13	0.05^{e}

[a] Solution (5 ml), approximately 0.1 *M* in duplicate. All yields in millimoles of product. [b] d = decalin, a = acetic acid. [c] Time left in bath, unrelated to rates. [d] Traces (~0.01 mmol) of 2,3-dimethylbutane. [e] In addition to 0.03 mmol of 2,3-dimethylbutane.

peresters prepared showed the characteristic infrared absorption (pentane solution) for a perester carbonyl group at 1770 cm^{-1}. Iodometric titration using the Silbert and Swern[69] procedure gave good results only with *t*-butyl peresters. *t*-Amyl and 2,3-dimethyl-2-butyl peresters gave low titers although infrared, nmr, and elemental analysis showed that they were pure. 2,3,3-Trimethyl-2-butylperoxy acetate was prepared on a small scale for esr studies from 2,3,3-trimethyl-2-butyl hydroperoxide (0.4 g) and acetyl chloride. The product was not distilled but infrared analysis indicated that it was pure.

Photolysis of Peresters. The photolyses were carried out in a Rayonet RPR-100 photochemical reactor (The Southern New England Ultraviolet Co.). Sixteen 2537-Å region lamps were employed. Aliquots (5 ml) of a 0.1 *M* solution of the perester were transferred from a standard flask to 15 × 1.5 cm quartz tubes. The solution, and the free space above the solution, were purged of oxygen by sweeping with a slow stream of helium for 5–10 min. After the tube was sealed tightly with a rubber septum, it was placed in the photochemical reactor which maintained an ambient temperature of 30 ± 1°. The tubes were rotated using a Rayonet MGR-100 merry-go-round. The progress of the reaction could be followed by carbon dioxide evolution and, in general, the reactions were complete in approximately 1 hr.

Aliquots (5 ml) of a 0.1 *M* solution of *t*-butylperoxy cyclopropylacetate in decalin were photolyzed to various degrees of conversion and then excess sodium methoxide in methanol was added and the mixture refluxed 1 hr. The mixtures were then analyzed for methyl cyclopropylacetate and methyl allylacetate. The experiments were repeated using pentane and Nujol as solvent. It was shown in separate experiments that for the amount of methyl cyclopropylacetate recovered 1% of the isomeric methyl allylacetate could be detected. It was also shown in separate experiments that the perester could be converted almost quantitatively to the methyl ester of the carboxylic acid under these conditions.

Table XIII. Quantum Yields for Carbon Dioxide Formation at 2537 Å

Perester $RCO_2OC(CH_3)_2R'$ R	R′	Concn, *M*	Solvent	CO_2[a]
CH_3	CH_3	0.10	Decalin	1.00
CH_3	CH_3	0.30	Decalin	1.02
CH_3	CH_3	1.0	Decalin	1.02
CH_3	CH_3	3.0	Decalin	1.12
CH_3	CH_3	~8 (neat)		1.28 (1.02)[b,c]
CH_3	CH_3	0.3	Pentane	1.02 (0.82)[b]
CH_3	CH_3	0.30	Decalin	0.97
CH_3	CH_3	0.30	Nujol	0.94
CH_3CH_2	CH_3	0.30	Decalin	0.96
$(CH_3)_2CH$	CH_3	0.30	Decalin	1.0
$(CH_3)_3C$	CH_3	0.30	Decalin	0.96
c-C_3H_7	CH_3	0.30	Decalin	0.89
CH_3	CH_2CH_3	0.30	Decalin	0.99
CH_3	$CH(CH_3)_2$	0.30	Decalin	1.01
Ph	CH_3	0.30	Decalin	0.59

[a] Average of at least three determinations carried to approximately 5% completion using chloroacetic acid actinometer. [b] Using ferrioxalate actinometer. [c] Literature value, Φ_{CO_2} = 1.01 (ref 3).

Thermolysis of Peresters. The peresters listed in Table XII were thermally decomposed in approximately 0.1 *M* decalin solutions at 115°. Each ampoule was sealed with a gas-tight rubber septum. However, due to the elevated temperatures and prolonged heating, the analyses were not as accurate as those carried out on the photochemical reactions.

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Analytical Procedures. Gas chromatographic analysis procedures were described previously.[7] Gaseous products were analyzed at room temperature on either a 2-ft Porapak Q or a 15-ft 30% Dowtherm on firebrick; C_5–C_3 hydrocarbons on a 12-ft SF 96 column at 80°; acetone, *t*-alcohols, and *t*-alkyl ethers on a 9-ft FFAP at 90°, a 12-ft didecyl phthalate column at 100°, a 12-ft SF 96 at 135°, and an 8-ft Carbowax 20M column at 40°. Mixtures of the cyclopropylcarbinyl, homoallyl and cyclobutyl ethers, and alcohols were analyzed on all four of the above columns. Carboxylic acids were analyzed on a 4-ft XF 1150 column at 200°. Methyl esters of cyclopropylacetic, cyclobutanecarboxylic, and allylacetic acids were analyzed on a 12-ft didecyl phthalate column at 140°.

Quantum Yield Measurements. Aliquots (3 ml) of a 0.3 *M* solution of perester were transferred from a standard flask to 10 × 1 cm tubes. The solutions were degassed with a slow stream of helium and the tubes tightly sealed with rubber septa. The solutions were photolyzed in a merry-go-round apparatus (F. Moses Co., Wilmington, Del.) which maintained an ambient temperature of 28° in the reaction cell. Aliquots (3 ml) of degassed solutions of the actinometer (either chloroacetic acid or potassium ferrioxalate) were photolyzed at the same time as the perester solutions. The reaction was allowed to proceed to about 5% conversion (approximately 30 min) and the yield of carbon dioxide was determined by gas chromatography. A value of 0.34 was used for the quantum yield of chloride ion from chloroacetic acid[70] and a value of 1.25 for the quantum yield of ferrous ion from potassium ferrioxalate.[71] There was negligible dark reaction for the peresters under these conditions. A helical low-pressure mercury resonance lamp[72] was used as the light source and the quartz tubes were covered with aluminum foil except for the window being irradiated. The relative values of the quantum yields listed in Table XIII are accurate to within at least 10%, but the absolute values may be less reliable.

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Kinetics of the Formation of N-Isobutylidenemethylamine from Isobutyraldehyde and Methylamine in Aqueous Solution[1]

Jack Hine, Francis A. Via, Judith K. Gotkis, and John C. Craig, Jr.

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received January 29, 1970*

Abstract: Stopped-flow spectrophotometric measurements on the reaction of isobutyraldehyde with methylamine in water at 35° over the pH range 10.1–11.5 gave a value of 8.5 ± 0.5 M^{-1} for K_{ca}, the equilibrium constant for addition of the amine to the aldehyde, and a value of 6.2 ± 0.7 $\sec^{-1}$ for k_c, the rate constant for dehydration of the carbinolamine to N-isobutylidenemethylamine. Kinetic studies of methylammonium chloride catalysis of the oximation of isobutyraldehyde at pH 8.5–9.8 gave values of $k_c K_{ca}$ in agreement with the stopped-flow measurement, but at pH 7.6 larger values were obtained, suggesting acid catalysis of the dehydration of the carbinolamine. The equilibrium constant for the addition of hydroxylamine to isobutyraldehyde was found to be 105 ± 11 M^{-1}, and the rate constant for dehydration of the adduct to give oxime fit the equation $k_d = (6.5 \times 10^5[H^+] + 3.2 \times 10^{-12}/[H^+] + 4.6 \times 10^{-3})\ \sec^{-1}$. A kinetic study of the hydration of isobutyraldehyde in the presence of N-methylmorpholine buffers showed that the reaction was fast enough that the hydration–dehydration equilibrium could be treated as continually established throughout the studies of the reaction of isobutyraldehyde. Structural effects on equilibrium constants for addition to isobutyraldehyde are discussed.

The kinetics and mechanism of the formation and hydrolysis of a number of imines derived from aromatic carbonyl compounds and/or aromatic amines have been studied previously. Many of these and similar studies of oximes, hydrazones, semicarbazones, etc., have been reviewed by Jencks.[2] Several studies of imines derived from acetone[3,4] and from aliphatic amino acids and keto acids[5] have been carried out. We are aware of no previous studies of the kinetics of the formation or hydrolysis of an unsubstituted aliphatic aldimine, but the studies of Stewart and coworkers on formocholine[6] and on iminium ions[7] are closely related. Such a study on an aldimine was needed in connection with studies of the deuterium exchange of isobutyraldehyde-2-*d* in the presence of primary amine salts.[8] These amine salts appear to catalyze the exchange by forming iminium ions that lose deuterium to some base in the rate-controlling step of the reaction (eq 1). In

$$\mathrm{Me_2CDCHO + RNH_3^+ \rightleftharpoons Me_2CDCH{=}NHR^+ \rightleftharpoons Me_2CDCH{=}NR + H^+}$$

$$\mathrm{Me_2CDCH{=}NHR^+ + B \longrightarrow Me_2C{=}CHNHR + BD^+} \quad (1)$$

order to understand this reaction more completely, in particular to learn under what conditions, if any, a change in the rate-controlling step may be expected, a knowledge of the kinetics and mechanisms of the imine-forming reaction is necessary. We have there-

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