a 1:1 mixture of 1-hexene and cyclohexane in tetrahydrofuran (with and without sensitizers) was irradiated at the same time. The samples were photolyzed for 168 hr at 27°. The reaction products were analyzed without solvent removal on a 6-ft column of 20% SF-96 on Chromsorb P at 50°. The concentrations of 1-hexene and cyclohexane formed in the two photochemical transformations were determined by comparisons of product peak areas (glpc) with those of known concentrations of the two hydrocarbons. Injection of known concentrations of 1-hexene and cyclohexane indicated 90% reaction after 168 hr.

Direct and Sensitized Photolyses of cis- and trans-3,8-Dimethyl-1,2-diaza-1-cyclooctenes 1 and 2 (R = CH₃). The results of the irradiation studies of mixtures of **1** and **2** (R = CH₃) under direct and photosensitized conditions are given in Table II. These experiments were conducted in the same fashion as for cis-1,2-diaza-cyclooctene (**3**). In this case, the concentration of **1** and **2** (R = CH₃) was 45 mg (0.300 mmol) in 1 ml of solution. After 345 mg (2.08 mmol) of fluorene was added to one tube, the samples were irradiated for 168 hr at 19°. Analyses (glpc) of the hydrocarbon mixtures were performed on a 6-ft column of 20% SF-96 on Chrom-

sorb P at 25° and on a 6 ft column of 5% QF-1 on Chromsorb W at 45° without solvent removal. Concentrations of products were determined from comparisons of peak areas with those obtained by injections of known amounts of the four hydrocarbons.

Direct and Sensitized Photolyses of trans-3,8-Diphenyl-1,2-diaza-1-cyclooctene 2 (R = C₆H₅). The photochemical reactions of **2** (R = C₆H₅) were conducted as that described above. Into each of two Pyrex tubes containing 2 ml of tetrahydrofuran was added 57 mg (0.232 mmol) of trans-3,8-diphenyl-1,2-diaza-1-cyclooctene **2** (R = C₆H₅). The samples were irradiated at 0° for 37 hr after 83 mg (0.460 mmol) of benzophenone had been added to one of the tubes. The photolytic solutions were analyzed on a 6-ft FFAP column at 220°. Comparisons of retention times were made with those of authentic samples.[10] Ultraviolet analyses of irradiated samples of **2** (R = C₆H₅) at different time intervals indicated no cis→trans isomerization of the azo linkage taking place.

Polar and Radical Paths in the Decomposition of Diacyl Peroxides[1]

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Abstract: The effect of solvents has been determined on the rates and products of decomposition of several diacyl peroxides, which decompose rapidly by presumed concerted scission of two bonds to yield a mixture of "polar" and "radical" products. Decomposition rates increase markedly in going from cyclohexane to acetonitrile, and the increase is accompanied by smaller decreases and increases respectively in yields of radicals scavenged by galvinoxyl and in polar products (including, in acetonitrile amides and imides from attack on solvent). On the basis of these results and literature data it is proposed that in these systems all products arise via a single rate-determining transition state, and product distributions are determined by the partitioning of a subsequent intimate ion pair–radical pair. The same formulation is suggested for a variety of cases of molecule-induced homolyses, anchimerically assisted homolyses, and radical rearrangements which show large polar effects and frequently strong solvent dependence.

When induced chain processes are eliminated, diacyl peroxides (RCOO)₂, R = phenyl or primary alkyl) decompose thermally by simple bond homolysis at similar rates which are almost solvent independent. Although there are kinetic complications due to

$$(RCOO)_2 \longrightarrow 2RCOO\cdot \longrightarrow 2R\cdot + 2CO_2 \qquad (1)$$
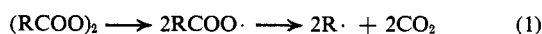
cage recombination of the primary fragments,[3,4] the chief differences lie in the rate of the second step, β scission to yield R· and CO₂.[5]

In contrast, peroxides in which R is a secondary or tertiary alkyl or a resonance-stabilized fragment such as benzyl decompose much more rapidly,[6,7] presumably

by a concerted process involving breakage of two or more bonds. Further, rates are now often highly solvent dependent and increase with solvent polarity.[8] It was early noted that such peroxides give relatively high yields of ester in which the stereochemistry of the alkyl portion is conserved.[9,10] More recently several groups[11,12] have shown that the ester is not a primary product, but arises from decomposition of an acyl carbonic anhydride, the "carboxyl inversion product" (eq 2). Such carboxyl inversion products

$$(RCOO)_2 \longrightarrow ROCOOCR \longrightarrow ROCOR + CO_2 \qquad (2)$$
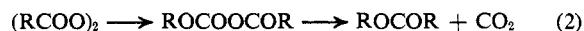
were first detected in highly asymmetric peroxides[13] and are generally considered to be the consequences of typical electron-deficient rearrangements.

(1) Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) To whom inquiries should be addressed at the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.

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

(4) J. W. Taylor and J. C. Martin, *J. Amer. Chem. Soc.*, **88**, 3650 (1966).

(5) For general discussion, cf. C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1956, Chapter 10.

(6) P. D. Bartlett and J. E. Leffler, *J. Amer. Chem. Soc.*, **72**, 3030 (1950).

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

(8) R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *J. Amer. Chem. Soc.*, **87**, 3928 (1965).

(9) M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **19**, 1283 (1955).

(10) H. H. Lau and H. Hart, *J. Amer. Chem. Soc.*, **81**, 4897 (1959).

(11) F. D. Greene, H. P. Stein, C. C. Chu, and F. M. Vane, *ibid.*, **86**, 2080 (1964).

(12) C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, Jr., *ibid.*, **87**, 518 (1965).

(13) J. E. Leffler, *ibid.*, **72**, 67 (1950).

Since these peroxides also yield scavengable radicals most workers have treated the overall decompositions as occurring through competing ionic and radical paths.

The goal of the work reported here was to examine the solvent and structural dependence of this competition, initially with isobutyryl peroxide, which had already been studied by Lamb in less detail,[8] and then with additional diacyl peroxides. Our general conclusion is that no complete dichotomy can be demonstrated between "polar" and "radical" decompositions, and, indeed, that they both probably proceed through the same rate-determining step to yield a transient intimate ion-paired spin-diradical intermediate.

Results

Isobutyl Peroxide. Decomposition rates were determined in several solvents and are summarized in Table I. Individual experiments gave good first-order plots,

Table I. Decomposition of Isobutyryl Peroxide at 40° [a]

Solvent	$k \times 10^5$, sec^{-1}
Gas	~1
Cyclohexane	4.70, 4.72,[b] 4.5[d]
Nujol	4.63, 4.64[c]
Benzene	23.8, 24.0,[c] 24.0[d]
Acetonitrile	68.1, 68.5[b]

[a] 0.033 M. [b] In presence of 0.5 M methyl methacrylate. [c] In presence of 0.1 M methyl methacrylate. [d] From ref 8.

and the absence of any effect of methyl methacrylate on rate shows that induced decomposition is unimportant in these systems. Our data in cyclohexane and benzene are also in good agreement with those of Lamb.[8]

Several scavengers were investigated in cyclohexane for the determination of radical yields, Table II. Al-

Table II. Comparison of Scavengers in Isobutyryl Peroxide Decomposition[a]

Scavenger	% radicals scavenged	
DPPH[b]	21.4	24.6
Koelsch's radical[c]	21.7	22.3
I₂	32.2	32.8
Galvinoxyl	41.2	43.6
	39.8	40.4

[a] In cyclohexane at 40°. [b] Diphenyl picryl hydrazyl. [c] α,γ-Bis(biphenylene)-β-phenylallyl.

though all gave satisfactory zero-order plots over small extents of peroxide decomposition, and good reproducibility, agreement between different scavengers is poor.[14] Galvinoxyl was chosen for further work since it gave the highest values and good material balances.

Products of decomposition were determined in the presence of enough galvinoxyl to scavenge all radicals escaping from the solvent cage and are listed in Table III. Yields of carboxyl inversion product and ester were also compared in acetonitrile at different temperatures and when the peroxide was decomposed by photolysis, Table IV.

(14) When compared in the same solvents our scavenger experiments are in only qualitative agreement with Lamb's.[8] Thus in CCl₄ with galvinoxyl his group reports a scavenging efficiency of 49.5% at 45°; we obtain 37.4 and 38.9 at 40°.

Table III. Products of Isobutyryl Peroxide Decomposition, 40° [a]

Solvent	Cyclo-hexane	Nujol	Benzene	Aceto-nitrile
Scavenged radicals[d]	41.5	17.0	24.6	10.2
Carboxyl inversion[c]	17.9	24.3	30.2	34.3
Ester	5.7	5.1	11.5	10.7
2,3-Dimethylbutane	25.1	38.4		1.1
Propylene	4.1	9.2		6.6
Propane	3.7	9.8		0.3
Other				38.7[b]
Balance	98.0	103.8		101.9

[a] Yields calculated in per cent based on two fragments/peroxide molecule. [b] Isobutyric acid, 22.1%; N-isopropylacetamide, 16.6%. [c] Isobutyl isopropyl carbonate. [d] From galvinoxyl consumption in separate experiments.

Table IV. Isobutyryl Peroxide. Carboxyl Inversion Product and Ester Yields in Acetonitrile

Conditions	% carboxyl inversion	% ester
20°	29.2	
40°	34.3	5.7
70°	36.5	
40°, direct photolysis	7.4	2.0
40°, sensitized photolysis[a]	0	1.7

[a] In presence of benzophenone.

The results listed in Table I and III confirm previous observations on isobutyryl and similar peroxides. Decomposition rates and yields of carboxyl inversion and other "polar" products increase with solvent polarity while scavengable radicals and radical-cage products (dimethylbutane, propane, and propylene) decrease. When results in cyclohexane and Nujol (solvents of similar polarity but differing viscosity) are compared we see no effect on rate and little on formation of carboxyl inversion product, but a large drop in scavengeable radicals and increase in radical-cage products: results expected if decarboxylation of isobutyryloxy radicals is fast compared to diffusion from the solvent cage.

In acetonitrile, formation of N-isopropylacetamide, isobutyric acid, and excess propylene indicates alternate paths in this solvent for the formation of polar products, and the results can be rationalized in terms of a β elimination and a modified Ritter reaction. Additional

$$(CH_3)_2CHC\overset{O}{\underset{O-O}{\underset{\displaystyle|}{\big\langle}}}\overset{O}{\overset{\displaystyle\|}{C}}-CH(CH_3)_2 \longrightarrow$$

$$(CH_3)_2C\overset{+}{H}\begin{matrix}O\\ \|\\ C\\ \|\\ O\end{matrix}\ \ ^-OCOCH(CH_3)_2 \quad (3)$$

$$\mathbf{I}$$

$$\mathbf{I} \longrightarrow C_3H_6 + CO_2 + (CH_3)_2CHCOOH \quad (4)$$

$$\mathbf{I} + CH_3CN \longrightarrow$$

$$(CH_3)_2CH-N=C\overset{\displaystyle CH_3}{\underset{\displaystyle OCOCH(CH_3)_2}{\big\langle}}\ + CO_2 \quad (5)$$

$$\mathbf{II}$$

$$\mathbf{II} \xrightarrow{\text{work-up}} (CH_3)_2CHNHCOCH_3 + (CH_3)_2CHCOOH \quad (6)$$
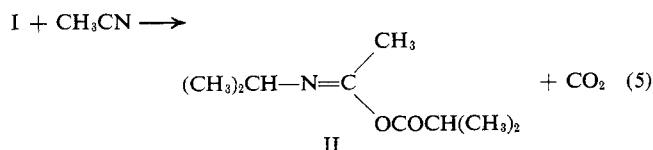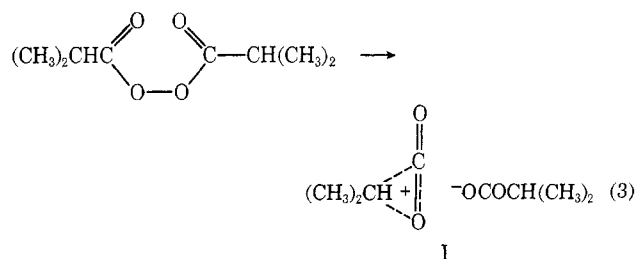
examples of this sort of process appear later,[15] but here we note that there is good agreement between yields of acid, 22.1%, and amide plus propylene in excess over propane, 22.9%. Finally, the low yield of polar products in photodecompositions parallels previous results and provides further conformation of our suggestion (discussed further below) that photolysis favors the formation of radical products in systems which give both polar and radical products on thermal decomposition.[16]

Other Peroxides. Four other peroxides were investigated in less detail. Mixed m-chlorobenzoyl acyl peroxides, R = alkyl, have been shown by Denney and Sherman[17] to give high yields of alcohol, ROH, on work-up presumably via a carboxyl inversion path. Our results with m-chlorobenzoyl isobutyryl peroxide and also unsubstituted benzoyl isobutyryl peroxide appear in Table V. Although decomposition rates are
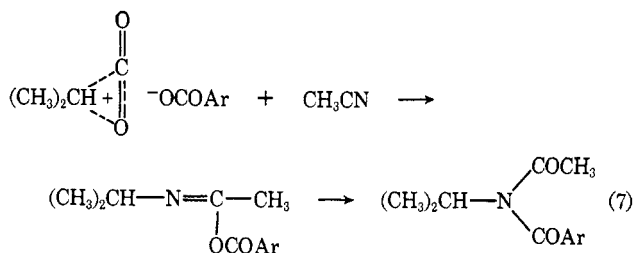
Table V. Decomposition of m-Chlorobenzoyl Isobutyryl Peroxide and Benzoyl Isobutyryl Peroxide

m-Chlorobenzoyl	Cyclohexane	Acetonitrile
$k \times 10^5$, sec^{-1} (41°)	4.40	103
Scavengable radicals	<1%	<1%
Carboxyl inversion	60.4	27.8
Ester	10.6	~2
Acid[b]	28.2	~2
Other		67[c]
Balance	99.2	98.8
Benzoyl		
$k \times 10^5$, sec^{-1} (41°)	1.63 (30.5)[a]	40.6
Scavengable radicals	<1%	<1%
Carboxyl inversion	62.5 (44.4)[a]	43.5
Acid[b]	35.2 (35.7)[a]	14.3
Other		39.8[c]
Balance	97.7	97.4

[a] At 70°. [b] m-Chlorobenzoic and benzoic acids, respectively. [c] N-Acetyl, N-m-chlorobenzoyl (or benzoyl) isopropylamine, see text.

comparable to isobutyryl peroxide, with neither peroxide do we find appreciable yields of scavengable radicals. In acetonitrile both show extensive reaction with solvent, here to give N,N-diacylisopropylamine, presumably via a modification of reaction sequence (eq 3-6), a possibly useful synthetic procedure. In

$$(CH_3)_2CH + \overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{C}} \quad {}^-OCOAr \quad + \quad CH_3CN \longrightarrow$$

$$(CH_3)_2CH-N\overset{+}{=}C-CH_3 \longrightarrow (CH_3)_2CH-N\overset{COCH_3}{\underset{COAr}{\diagdown}} \quad (7)$$
$$\underset{OCOAr}{|}$$

the hope of investigating the sterochemistry of eq 7, the decomposition of 4-t-butylcyclohexylformyl m-chlorobenzoyl peroxide was examined. In cyclohexane $k_{41} = 3.83 \times 10^{-5}$ sec^{-1}, but our goal was frustrated

(15) F. D. Greene, Jr. (private communication), has also observed similar products in acetonitrile with other peroxides.
(16) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3413 (1965).
(17) D. B. Denney and N. Sherman, *J. Org. Chem.*, **30**, 3760 (1965).

since it gave 86.4 and 84.8% carboxyl inversion product in cyclohexane and acetonitrile and only a trace (3.8%) of products hydrolyzing to amine in the latter.

α-Chloropropionyl m-chlorobenzoyl peroxide, with an electronegative substituent on its alkyl group should show less tendency to undergo carboxyl inversion. Results here were less clear because of some apparent induced decomposition and because HCl liberated in the decomposition reacts with galvinoxyl so that scavenging experiments had to be carried out in the presence of pyridine. Results appear in Table VI, and signifi-

Table VI. Decomposition of α-Chloropropionyl m-Chlorobenzoyl Peroxide (41°)

Conditions	$k \times 10^5$, sec^{-1}	Scavengable radicals (%)
Cyclohexane	2.93	(43)
Cyclohexane + 0.1 M MM[a]	1.51	
Cyclohexane + 0.025 M pyridine	2.91	25
Acetonitrile	3.63	30
Acetonitrile + 0.1 M MM[a]	3.05	
Acetonitrile + 0.025 M pyridine	3.08	21

[a] Methyl methacrylate.

cant radical formation is indicated. Products were not examined in detail but ir spectra of reaction mixtures of cyclohexane indicated 10-20% carboxyl inversion product.

Finally, we have examined peroxides which decompose rapidly at room temperature or below. Our data on phenylacetyl peroxide appear in Table VII, and

Table VII. Decomposition of Phenylacetyl Peroxide at 20°

Solvent	$k \times 10^5$, sec^{-1}	Scavengable radicals (%)
Cyclohexane	16.0	47
CCl$_4$	18.6	56
Benzene	47.6	30
Acetonitrile	102	10

again we find that rates increase and radical yields decrease with increasing solvent polarity, much as with isobutyryl peroxide. Ir spectra of reaction mixtures indicated the presence of carboxyl inversion product, but we were unable to prepare samples of benzyl phenylacetyl carbonate for comparison for quantitative analysis. Attempts to investigate pivaloyl peroxide were also unsuccessful, since it decomposed in solution too rapidly for kinetic measurement even at 0°.

Discussion

The objective of this study was to examine the effect of structure and solvent on the rate of decomposition of diacyl peroxides and on the partitioning between "radical" and "polar" products. Our results, together with some from the literature, are summarized in Table VIII. As "polar" products in our own work we have counted carboxyl inversion products, free acid

Table VIII. Summary of Decomposition Data on Peroxides

Compd	R₁	R₂	Solvent	T, °C	$k \times 10^5$	% polar products
1	Isopropyl	Same	Cyclohexane	40	4.7	18
			Benzene	40	24	30
			Acetonitrile	40	68	78
2	Isopropyl	m-Cl-phenyl	Cyclohexane	41	4.4	100
			Acetonitrile	41	103	100
3	Isopropyl	Phenyl	Cyclohexane	41	1.6	100
			Acetonitrile	41	40.6	100
4	2-Cl-isopropyl	m-Cl-phenyl	Cyclohexane	41	1.5	Some
			Acetonitrile	41	3	Some
5	Benzyl	Same	Cyclohexane	20	16	Some[i]
			Benzene	20	48	Some
			Acetonitrile	20	102	Some
6	Cyclohexyl	Same	CCl₄	40	5.2	52[a]
7	exo-2-Norbornyl	Same	CCl₄	45	7.2	45[b]
8	endo-2-Norbornyl	Same	CCl₄	45	0.9	53[c]
9	cis-4-t-Butylcyclohexyl	Same	CCl₄	40	8.7	90[d]
10	trans-4-t-Butylcyclohexyl	Same	CCl₄	40	4.3	90[d]
11	Triptyl	Same	Benzene	80	14.2	72[e]
12	1-Apocamphyl	Same	CCl₄	80	23	50[f]
13	Phenyl	Benzyl	Benzene	25	20.5	>90[g]
14	α-Phenylethyl	Same	Ether	0	Fast	48[h]

[a] 12% acid, 40% ester,[i] later shown to arise from carboxyl inversion product,[11] combined with other rate data.[10] [b] 20% ester, 25% acid.[k] [c] 30% ester, 32% acid.[k] [d] Ester reported,[10] later shown to be chiefly carboxyl inversion product.[12] [e] 61% acid plus 11% ester on work-up (34% alcohol also present).[l] [f] 50% ester,[m] combined with other rate data.[l] [g] Ester, carboxyl inversion product, and diphenylmethane major products, 6.6% scavengable radicals.[n] [h] 37% ester (with 84% retained stereochemistry), 5% α-phenylethanol, 6% styrene.[o] [i] In CCl₄ at 40°, decomposition yields 24% carboxyl inversion product, unpublished work by Dr. A. R. Lepley. [j] R. C. Lamb and J. G. Pacifici, *J. Amer. Chem. Soc.*, **86**, 914 (1963). [k] H. Hart and F. R. Chloupek, *ibid.*, **85**, 1155 (1962). [l] P. D. Bartlett and F. D. Greene, *ibid.*, **76**, 1088 (1954). [m] M. S. Kharasch, F. Engelman, and W. H. Urry, *ibid.*, **65**, 2428 (1953). [n] T. Suehiro, S. Hibino, and T. Saito, *Bull. Chem. Soc. Jap.*, **41**, 1707 (1968). [o] F. D. Greene, *J. Amer. Chem. Soc.*, **77**, 4869 (1955).

(assumed to arise *via* processes equivalent to eq 4), and products of attack on acetonitrile. Since most of the literature data were obtained before the importance of carboxyl inversion was recognized and involved product determination after long heating which converts most carboxyl inversion product to ester, we have counted ester and free acid plus any other obvious polar products.[18]
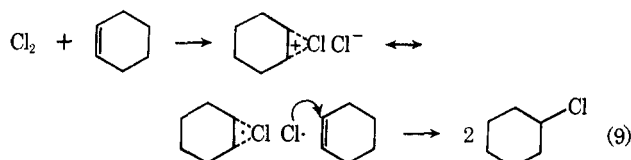
Inspection of Table VIII permits three generalizations. (1) In spite of enormous variations in decomposition rate (*cf.* **12** and **14**), all peroxides listed show significant yields of polar products, even in nonpolar solvents. (2) In the same solvent peroxides with similar decomposition rates which might be expected to produce radicals of similar stability (*cf.* **1**, **4**, **6–10**) show widely different yields of polar products. (3) Where investigated (*cf.* particulary **1**), total decomposition rates and ratios of polar to radical products both increase with solvent polarity, but the former more rapidly. In short, formation of both types of product are accelerated. Since our own work was completed, a further example of several of these phenomena has been reported by Lamb and Sanderson[19] who have examined the decomposition of a number of ring-substituted benzoyl isobutyryl peroxides, chiefly in cyclohexane. Their results are too extensive to be

(18) Esters are also formed, presumably *via* cage recombination, from peroxides for which there is no evidence for concerted bond scission or the formation of polar type products (*e.g.*, acetyl and propionyl peroxides). However yields are generally low (<20%) particularly in non-viscous solvents. Since there is no way for correcting for such a contribution, and since decarboxylation of the acyloxy radicals formed from α-branched peroxides should be particularly rapid, we have not attempted any correction.

(19) R. C. Lamb and J. R. Sanderson, *J. Amer. Chem. Soc.*, **91**, 5034 (1969). Their product studies are in good agreement with ours except that they find low (1–17%) but appreciable yields of scavengeable radicals, particularly at higher temperatures.

included in Table VIII, but electron-withdrawing groups considerably increase decomposition rates (at 60° $pNO_2/pOCH_3$ = 8.7), slightly increase the yield of carboxyl inversion products, and decrease yields of scavengeable radicals. To accommodate these results in terms of two parallel independent paths, one leading to radical and the other to polar products seems to us to ask too much of coincidence, and we propose as a more economical hypothesis that all products arise *via* a single rate-determining step; a common transition state, in which the "radical" or "ionic" nature of the reaction has not been established. Beyond this point they pass to an "intimate" or "tight" ion pair–radical pair intermediate in which electronic interaction between the fragments is still extensive and ionic and paired diradical formulations merely represent contributing structures of a resonance hybrid. As these fragments become separated by solvent, or perhaps undergo rotation in solution, ionic and radical structures represent increasingly distinct species, interconvertable *via* oxidation–reduction. On the same time scale as this separation interconversion between paired and unpaired (triplet) radical pairs also begins to take place, Scheme I. The steps illustrated in Scheme I must all occur extremely rapidly, representing as they do processes taking place within the solvent cage. Polar products probably form at the "intimate ion pair–radical pair" stage, since, in a relatively symmetric peroxide one would expect a solvent separated ion pair to be less stable than the two corresponding radicals. Separation of a second molecule of CO_2, although not specified in the scheme, must also be very fast and competitive with solvent separation, since on going from cyclohexane to Nujol isobutyryl peroxide shows a large increase in yield of 2,3-di-

Scheme I

$$\underset{\substack{\| \\ RC}}{O}-O-\underset{\substack{\| \\ CR}}{O} \;\rightleftharpoons\; R\cdots\underset{\substack{\| \\ C}}{O}=O\cdots O-\underset{\substack{\| \\ CR}}{O} \;\rightleftharpoons\; R\underset{+}{\cdots}C\mathord{\uparrow}O-\underset{\substack{\| \\ CR}}{O}$$

$\downarrow \longrightarrow$ polar products

"intimate" pair $R\cdot\downarrow\overset{O}{\underset{O}{C}}\uparrow\cdot O-\overset{O}{CR}$

$\nearrow\!\!\!\!/$

$\underset{\text{polar products?}}{\overset{CO_2^-OCOR}{R^+\nearrow}} \;\overset{?}{\rightleftharpoons}\; R\cdot\uparrow CO_2\downarrow\cdot OCOR$

separated pair $\longrightarrow$ radical products

$\nwarrow\!\!\!\!\backslash$

$R\cdot\uparrow CO_2\uparrow\cdot O\overset{O}{CR}$

triplet

methylbutane but not of ester. Further, the low yield of "radical" cage products in acetonitrile arises because the "intimate" pair goes chiefly to "polar" products. In the scheme we have indicated spin inversion to yield a triplet radical pair as competing with other solvent-separated processes, but it may also occur within the intimate ion–radical pair.[20] This has bearing on the details of the photochemical dissociation which, if it occurs from a triplet state, should give rise to a triplet radical pair directly. Our own results—a small yield of carboxyl-inversion product on direct photolysis, but none in the benzophenone-sensitized reaction, Table IV—while too fragmentary to be conclusive, suggest that direct photolysis occurs from both singlet and triplet states and that little spin inversion from triplet pair to ion–radical pair occurs in this system.[21]

The basic idea in this interpretation, that the rate-determining bond scission may occur prior to product-determining steps which partition the reaction between "polar" and "radical" paths is simply an extension of the familiar concept of polar and radical contributions to the transition states of radical processes to the proposal that similar structures may contribute to at least the first metastable intermediate beyond the transition state—the intimate ion–radical pair. It thus should apply to other processes which yield mixed "polar" and "radical" products, and we feel, rationalizes a number of puzzling features of a wide variety of reactions commonly described as "molecule-induced homolyses" and "anchimerically assisted homolyses." Without attempting an exhaustive review, we cite a few examples.

A number of cases are known where peroxides undergo accelerated decomposition in the presence of suitable olefins, to yield reaction products with the olefin plus variable yields of scavengable radicals. Examples are the reaction of m-bromobenzoyl peroxide with dimethoxystilbene,[22] the anchimerically assisted decomposition of o-vinylbenzoyl peroxides and per-

benzoates,[23] and the accelerated decomposition of hydroperoxides in the presence of styrene. Thus in the last case yield of radicals available to initiate polymerization is only 1.6% with 0.2 M t-butyl hydroperoxide, the bulk of the reaction yielding t-butyl alcohol and styrene oxide.[24] We would now suggest that partitioning between the two paths occurs from a radical–ion pair after a common rate-determining transition state.

The most striking cases of anchimeric assistance occur with substituents having available electron pairs with the possibility of valence-shell expansion, e.g., in the decomposition of o-iodobenzoyl peroxide[25] and o-thiobenzoyl peresters,[26] and in the later case Bentrude and Martin[26] have in fact formulated the reaction essentially as we would here.

Another case with a common transition state and a transient intermediate which partitions into polar and radical products is in the reaction of diacyl peroxides with tertiary (and perhaps other) amines, e.g.[27]

$(C_6H_5COO)_2 + R_3N \longrightarrow$

$\quad [R_3NOCOC_6H_5]^+ + [C_6H_5COO^-] \longrightarrow$ products (8)

Interestingly we find that benzoylisobutyryl peroxide, which gives negligible yields of radicals on homolysis, gives significant quantities (14–25%) on reaction with dimethylaniline in hexane. Since propane (9.7%) and propylene (4.5%) are both produced, attack of the amine is evidently on the isobutyryl peroxide oxygen. Other products are m-chlorobenzoic acid (94%) and isobutyric acid (61%), the latter presumably from the polar decomposition of the intermediate.

Leaving peroxides, another example of molecule-induced homolysis is the spontaneous initiation of radical halogenation by halogens and alkyl hypochlorites in the presence of olefins. In the case of chlorine, Poutsma has shown that the initiation is at least second order in olefin[28] and our proposal would be that the intimate ion pair which is an intermediate in the ordinary polar addition in nonpolar solvents has

(20) For comments on the role of this sort of exchange in CIDNP nmr spectra, cf. G. L. Closs, J. Amer. Chem. Soc., 91, 4554 (1969).

(21) From the practical point of view, we conclude that both sensitized and direct photolysis are accordingly effective ways of generating radicals from peroxides which thermally give predominently "polar" products.

(22) F. D. Greene, W. Adam, and J. E. Cantrill, J. Amer. Chem. Soc., 83, 3461 (1961).

(23) T. Koenig and J. C. Martin, J. Org. Chem., 29, 1520 (1964).

(24) C. Walling and L. Heaton, J. Amer. Chem. Soc., 87, 38 (1965).

(25) W. Cooper, J. Chem. Soc., 3106 (1951); J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, J. Amer. Chem. Soc., 80, 5435 (1958).

(26) W. G. Bentrude and J. C. Martin, ibid., 84, 1561 (1962).

(27) For discussion cf. ref 5, p 590.

(28) M. L. Poutsma, J. Amer. Chem. Soc., 85, 3510 (1963).

enough radical character to attack another molecule of olefin, e.g.

$$Cl_2 + \text{[cyclohexene]} \rightarrow \text{[cyclohexyl]} \ddot{:}Cl \ Cl^- \longleftrightarrow$$

$$\text{[cyclohexyl]} \ddot{:}Cl \ Cl\cdot \ \text{[cyclohexene]} \rightarrow 2 \ \text{[cyclohexyl]}Cl \quad (9)$$

Since a diradical with paired spins in close proximity should have similar properties to our radical–ion pair, we believe our picture provides a plausible explanation for the several cases of diradical rearrangements involving 1,2 shifts of hydrogen or alkyl groups which have little or no analogy in simple radical chemistry.[29] The simplest case is the rearrangement of cyclopropane to propylene, but an interesting recent example involves the decomposition of a cyclic perester[30] in which alkyl

$$\text{[cyclic perester with R, C}_6\text{H}_5\text{]} \rightarrow \text{[R-C(=O)-O-C}_6\text{H}_5\text{]} + CO_2 \quad (10)$$
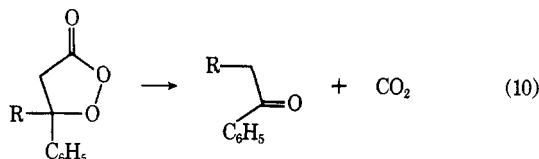
groups migrate in preference to phenyl. In our terms the migration is possible because the transition state is sufficiently dipolar to make the rearrangement essentially a carbonium ion process but it also should

$$\text{[R, C}_6\text{H}_5\text{ structure]} \longleftrightarrow \text{[R, C}_6\text{H}_5\text{ structure]} \quad (11)$$
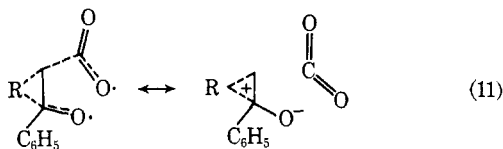
be recognized that the formation of a double bond from a diradical gives all of these rearrangements a very large driving force.

If a diradical is generated initially in a triplet state via a photochemical process, in our formulation the intersystem crossing to a singlet would have to precede rearrangement, as it would ring closure. The experimental situation here is still unclear, although the problem has been discussed by Schuster.[31]

(29) C. Walling in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., p 416.

(30) W. Adams and Y. M. Cheng, J. Amer. Chem. Soc., 91, 2109 (1969).

(31) D. I. Schuster and D. J. Patel, ibid., 90, 5145 (1968).

Finally several rearrangements, e.g., Stevens rearrangements of quarternary ammonium salts[32] and Meisenheimer arrangements of N-oxides,[33] which had been considered polar processes, have recently been shown to give products with chemically induced dynamic nuclear polarization of their nmr spectra, indicating radical intermediates. Again we suggest that these too may be proceeding through ion–radical pairs.

Experimental Section

Peroxides. Isobutyryl peroxide was prepared as described by Kharasch.[9] The product was distilled in vacuo at room temperature and stored as a standard solution in pentane. Solutions in other solvents were prepared by removing pentane from aliquots in vacuo and adding solvent. Other symmetric peroxides were prepared similarly, but were not distilled, and concentrations were determined by titration.

Benzoyl isobutyryl peroxides and other unsymmetric peroxides were prepared by reacting the aromatic peracid with isobutyryl chloride in hexane plus pyridine at 0°, extracting with dilute HCl and bicarbonate and purity determined by titration.

Carboxyl inversion products for reference were prepared by reacting the appropriate acid and chloroformate at −10 to− 55° in ether with pyridine and vacuum distilled or recrystallized.

N,N-m-Chlorobenzoylacetylisopropylamine was prepared by dissolving 3.09 g of N-isopropyl-m-chlorobenzamide in 25 ml of cyclohexane, adding 3.5 g of PCl_5, heating to boiling for 1 hr, and removing solvent in vacuo. The residual oil was added gradually to a stirred solution of 5.0 g of sodium acetate in 15 ml of water. After 1 hr the product was extracted with ether and purified by column chromatography, yield 85%.

Kinetic experiments were carried out in sealed, degassed tubes, and unreacted peroxide was determined by iodometric titration. For the gas-phase reaction the tubes were attached to bulbs into which the peroxide vaporized on warming.

Scavenger experiments were carried out by following scavenger disappearance spectrophotometrically, essentially as described by Bartlett.[34]

Product analyses were carried out by a combination of techniques. Carboxyl inversion products were determined by ir analysis using the 1805-cm^{-1} absorption, calibrated with synthetic material. Volatile products—hydrocarbon, esters, etc.—were determined by gas–liquid chromatography (glpc) using internal standards and known reference materials. Yields of ester were corrected for ester formed by decomposition of carboxyl inversion product during analysis. In the case of the mixed acyl benzoyl peroxides products were also separated by thin layer chromatography and the reaction products with acetonitrile isolated and determined quantitatively either by isolation or by saponification and determination of liberated amine. The quantities reported are probably good to within 5% of their reported values.

(32) U. Schöllkopf, U. Ludwig, G. Ostermann, and M. Patsch, Tetrahedron Lett., 1315 (1969).

(33) A. R. Lepley, P. M. Cook, and G. F. Willard, J. Amer. Chem. Soc., 92, 1101 (1970).

(34) P. D. Bartlett and T. Funahashi, ibid., 84, 2596 (1962).