Decomposition of Dicyclohexyl Peroxydicarbonate and OO-*t*-Butyl O-Cyclohexyl Peroxycarbonate
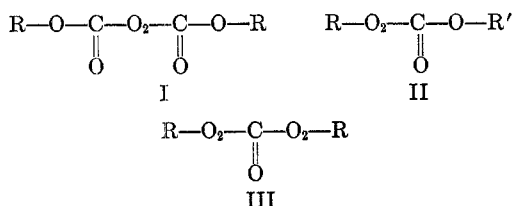
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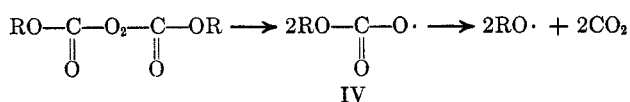
The decomposition of dicyclohexyl peroxydicarbonate (DCPD) in benzene solution proceeds both by thermolysis of the peroxide bond and by an induced mechanism, so that a rate law of the form $R_{DCPD} = k_1[DCPD] + k_i[DCPD]^{1/2}$ describes the kinetics. At 50°, the values of k_1 and k_i are 3.9×10^{-5} sec^{-1} and 1.39×10^{-4} $M^{-1/2}$ sec^{-1}, respectively, when analyses consist of measuring evolved carbon dioxide; slightly different values are obtained when titrimetric analysis is used for the peroxide. At 0.1 M, the amounts of DCPD decomposing by thermal and chain mechanisms will be about equal. The products from DCPD decomposition in benzene are carbon dioxide, cyclohexanol, and cyclohexanone, but others arise when cyclohexane, toluene, or α-methylstyrene is used as solvent. The greatly reduced yield of carbon dioxide in α-methylstyrene solvent and the absence of expected alkoxy radical fragmentation products from DCPD decomposition in other solvents suggest that intermediate alkoxycarboxyl radicals (IV) do not readily decarboxylate before entering into reactions with solvent or bimolecular disproportionation. When the alkoxycarboxyl radicals are produced at 110° from OO-*t*-butyl O-cyclohexyl peroxycarbonate (II, R = *t*-C$_4$H$_9$; R' = *c*-C$_6$H$_{11}$), there is some indication that partial decarboxylation can occur in benzene; however, decarboxylation still competes poorly with scavenging by α-methylstyrene solvent.

Diethyl peroxydicarbonate (I, R = C$_2$H$_5$) was apparently first described by Wieland, von Hove, and Borner[2] in 1925, but this class of peroxides, along with monopercarbonates (II) and dipercarbonates (III), was almost unknown until the publication of a definitive paper by Strain and coworkers.[3] Subsequent publications by McBay and coworkers[4] also reported on peroxy dicarbonate decompositions. These compounds have shown utility as initiators for polymerization of ethylene and other vinyl monomers, and have been investigated extensively by Russian scientists.[5] Our purpose in investigating the peroxydicarbonates was to determine the mechanism of their thermal decomposition and their suitability as sources of alkoxy radicals, which could be expected to arise from the sequence

$$RO-\underset{\underset{O}{\|}}{C}-O_2-\underset{\underset{O}{\|}}{C}-OR \longrightarrow 2RO-\underset{\underset{O}{\|}}{C}-O\cdot \longrightarrow 2RO\cdot + 2CO_2$$

IV

in analogy with diacyl peroxides as alkyl radical sources especially methyl radicals.[6] Forming alkoxy radicals from compounds easily synthesized from alcohols would offer great advantage over the use of primary or secondary dialkyl peroxides, which are relatively difficult to obtain. This paper will show that, in addition to the thermal O–O bond fission, there is an induced decomposition of dicyclohexyl peroxydicarbonate, and that the decarboxylation of the alkoxycarboxyl radical (IV) is negligible at 50° compared to reaction with solvent or bimolecular disproportionation. There is some evidence that decarboxylation of alkoxycarboxyl radicals formed from monopercarbonates becomes significant in the 100–110° range.

Experimental Section

Materials.—Dicyclohexyl peroxydicarbonate (DCPD) was prepared by Strain's[3] procedure. Cyclohexyl chloroformate and sodium peroxide were mixed at 0°, then stirred rapidly while being warmed to room temperature; the DCPD separated out in a semicrystalline mass. After trituration with 5% pyridine–water, the DCPD was recrystallized from methanol (dissolved at room temperature, crystallized at *ca.* −20°); mp 46° dec (lit.[3] mp 46°); titer,[7] 3.50 mmol of peroxide/g (theoretical, 1000/286.34 = 3.50 mmol/g).

OO-*t*-Butyl O-cyclohexyl peroxycarbonate (cyclohexyl *t*-butyl monopercarbonate) (CBMP) was prepared from cyclohexyl chloroformate and *t*-butyl hydroperoxide in the same manner as OO-*t*-butyl O-isopropyl peroxycarbonate; the procedure is described by Strain.[3] CBMP was obtained as an oil which could be distilled at 0.05 Torr with an apparent boiling point of 70°. Titration[7] showed the oil to contain 4.35 mmol of peroxide/g, compared to the theoretical value of 4.62 mmol/g. The infrared spectrum of the material shows a weak OH stretch at 2.25 μ, which suggests impurities, one of which is probably cyclohexanol. The carbonyl stretching frequency of the monopercarbonate group appears as an intense doublet at 5.60 and 5.70 μ.

Benzene was Matheson Coleman and Bell Chromatoquality, which was dried by boiling just before use. The toluene was Mallinckrodt Analytical Reagent, and the cyclohexane was Eastman Spectroquality. The α-methylstyrene was Eastman White Label material which was washed with aqueous sodium hydroxide, dried, and distilled before use.

Kinetic Procedure.—Most of the DCPD decompositions were done in a three-neck 100-ml flask connected to a Fisher Unitized gas buret assembly. The connection was made by a short length of water-jacketed tubing (circulating water *ca.* 5–10°) connected by a Swagelok connector to $^1/_{16}$-in.-o.d. stainless tubing, which was connected to the capillary glass tubing of the buret by another Swagelok connector. The reaction mixture was stirred by a magnetically driven bar. The flask was submerged

I   II

III

(1) Research Laboratories, Tennessee Eastman Co., Kingsport, Tenn. 37662

(2) H. Wieland, H. von Hove, and K. Borner, *Ann. Chem.*, **446**, 46 (1925).

(3) F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens, and J. H. Langston, *J. Amer. Chem. Soc.*, **72**, 1254 (1950).

(4) (a) H. C. McBay and O. Tucker, *J. Org. Chem.*, **19**, 869 (1954); (b) H. C. McBay, O. Tucker, and A. Milligan, *ibid.*, **19**, 1003 (1954); (c) H. C. McBay, O. Tucker, and P. T. Graves, *ibid.*, **24**, 536 (1959).

(5) (a) Z. I. Kulitski, L. M. Terman, V. F. Tsepalov, and V. Ya. S'hlyapintokh, *Izv. Akad. Nauk SSSR*, 253 (1963); *Chem. Abstr.*, **59**, 358 (1963); (b) A. A. Vichotinskii, *Zh. Fiz. Khim.*, **38** (6), 1668 (1964); *Chem. Abstr.*, **61**, 9007 (1964); (c) G. A. Razuvaev, L. M. Terman, and D. M. Yanovskii, *Vysokomol. Soedin.*, Ser. B, **9** (3), 208 (1967); Kresge-Hooker Science Library Services Translation, Order No. 18241; (d) G. A. Razuvaev, L. M. Terman, and V. A. Dodonov, *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva*, **11** (2) 202 (1966); Kresge-Hooker Science Library Services Translation, Order No. 16769b.

(6) C. Walling, "Free Radicals In Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 491.

(7) R. D. Mair and J. Graupner, *Anal. Chem.*, **36**, 194 (1964); method I was used.

TABLE I

DECOMPOSITION OF DICYCLOHEXYL PEROXYDICARBONATE AT 50°[a]

Run	[DCPD]₀,[b] M	$10^5 \times k_a$[c]	$(-d[DCPD]/dt)_0$,[d] M sec$^{-1} \times 10^7$	DCPD,[e] mmol	CO₂/2, mmol	Total reaction time, ksec	Final peroxide titration, M
68	0.01021	5.4	5.5	0.412	0.461	~80	
77	0.0248	6.4₅	16.0	1.002	1.043	71	
74	0.0485	7.0	34.0	0.974	0.936	86	
60	0.0972	8.1	78.7	1.958	1.904	78	
64	0.251	10.9	274	2.284	2.248	72	
109	0.0318	7.2₈[f]	23.2			20.9	0.0067
107	0.0983	9.33[f]	9.1₈			17.8	0.0174
111	0.2907	13.2[f]	384			15.8	0.0358
90[g]	0.0445			0.894	0.260	84	0.00062
113[g]	0.1025	5.9[f]	60.5			20.7	0.0284
80[h]	0.0492		~30[i]	0.996	0.77	98.	0.00097
87[j]	0.0519		~8.4[i]	0.517	0.477	84	0.0016

[a] Benzene solvent except as noted. [b] Initial concentration at 50° from weighed DCPD and solvent. [c] Apparent first-order rate constant; see text. [d] Initial rate corresponding to [DCPD]₀. [e] Estimated amount of DCPD in reaction flask when buret readings started. [f] Titrimetric determination. [g] PhC(CH₃)=CH₂ solvent. [h] c-C₆H₁₂ solvent. [i] Estimated from plots of CO₂ vs. t at initial stages of decomposition. [j] PhCH₃ solvent.

up to the neck in a constant-temperature bath kept at 50 ± 0.1°.

Solutions of DCPD in benzene, toluene, cyclohexane, or α-methylstyrene of 10–40 ml were made up in volumetric flasks and an aliquot was pipetted to the three-necked flask. Carbon dioxide was flushed through the apparatus for 100 sec while the solution was stirred at room temperature. Analysis of the effluent, trapped in toluene at −80°, showed loss of solvent to be negligible. The gas stream was shut off and the reaction flask was immersed in the bath. A thermal equilibration period of 500 sec was allowed before buret readings for the carbon dioxide liberated were started. Periodic readings were taken of carbon dioxide released, and an "infinity" point for total gas yield was determined. Some product solutions were saved for analysis.

Some DCPD decompositions were followed titrimetrically by delivering 10–25 ml of the solutions to a vessel[8] of ca. 50-ml capacity, shown in Figure 1. The solutions were degassed by three freeze–thaw cycles on the vacuum line, and the apparatus was pressured with ca. 900 Torr of nitrogen at −80°. The vessel was placed in the 50° bath and ca. 10 min was allowed for thermal equilibration before samples were taken for titration.[7]

CBMP and some DCPD solutions were decomposed in tubes equipped with breakseals. Solutions were delivered to the tubes, degassed, and maintained at 110° for ca. 20 hr. The evolved gas was analyzed by standard vacuum line techniques.

The solutions of decomposition products were analyzed on a Wilkens-Aerograph A90-P gas chromatograph. Carbowax 20 M was the usual stationary phase (15% on Chromosorb R) in the 15 ft × 0.25 in. columns, but tetracyanoethylated pentaerythritol (TCEPE) was used to separate α-methylstyrene, cyclohexanol, and cyclohexanone. Most effluent peaks were identified by comparing retention time with authentic samples; in a few cases, mass spectra of trapped effluent were obtained. Durene was added as an internal standard, and response factors were determined for the identified products. Dicyclohexyl monopercarbonate was assumed to be absent from the product solutions, since the peroxide titer was very low and the carbon dioxide yields were nearly quantitative. Dicyclohexyl peroxide was not specifically searched for and could be present if it does not elute under our glpc conditions.[8a]

Results

Table I summarizes kinetic data for the decomposition of DCPD at 50° in benzene and other solvents. The first five runs are from the gasometric analyses;

(8) The use of a sampling vessel of this type was described by A. Streitwieser, D. E. Van Sickle, and W. C. Langworthy, *J. Amer. Chem. Soc.*, **84**, 246 (1962).

(8a) NOTE ADDED IN PROOF.—Dr. R. R. Hiatt, Brock University, St. Catharines, Ont., informs me that no di-sec-butyl peroxide is formed from the decomposition of sec-butyl peroxydicarbonate.
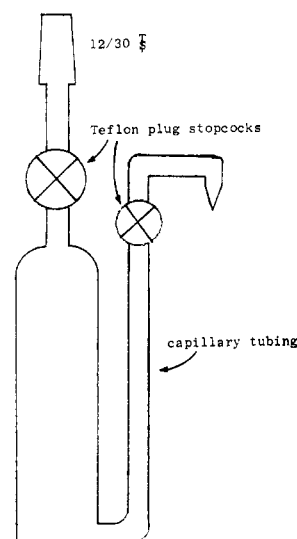
Figure 1.—Sampling vessel.

the next three are titrimetric analyses. Gas evolution data and a single titrimetric analysis of DCPD decomposition in other solvents are also shown in Table I. Tables II and III summarize the product data on DCPD and CBMP decompositions, respectively.

For gasometric determinations in benzene, it was assumed that 2 mol of carbon dioxide are liberated per mol of DCPD decomposed. Plots of log [DCPD concentration] vs. time were usually linear for several kiloseconds, and the listed apparent first-order rate constant, k_a, was obtained from the slope of the line. For titrimetric determinations, log [DCPD] vs. time plots were linear throughout the course of the reaction (up to 80% decomposition). For decompositions in cyclohexane and toluene, the carbon dioxide–DCPD stoichiometry of the decompositions in benzene was assumed; initial rates were obtained directly by plotting the first few DCPD concentrations against the corresponding times. The titrimetric measurement of DCPD decomposition in α-methylstyrene gave a good first-order plot, but carbon dioxide yield from the gasometric run was too low for the stoichiometry assumption to be used.

Discussion

Dicyclohexyl Peroxydicarbonate Decomposition.—
That the decomposition of DCPD in benzene is not simply first order is apparent from inspection of the "first-order" rate constants, k_a, in Table I. For the first five runs, the rate constant approximately doubled for a 25-fold increase in DCPD concentration. A simple rationalization of the results follows that developed by Nozaki and Bartlett for benzoyl peroxide.[9] The simplicity of the products also supports the mechanisms shown in eq 1–3 for the decomposition in the initial stages.

Here, it is proposed that the induced decomposition involves abstraction of an α-hydrogen on the cyclohexane ring. Strain mentioned the likelihood of induced decomposition in peroxydicarbonate decompositions,[3] but the Russian workers seem to discount this possibility.[5]

Application of the usual steady-state assumption to reactions 1–3 gives

$$\frac{-d[\text{DCPD}]}{dt} = k_1[\text{DCPD}] + k_2\left(\frac{k_1}{k_3}\right)^{1/2}[\text{DCPD}]^{3/2} \quad (4)$$

(9) K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.*, **68**, 1686 (1946).

and with some quantities redefined

$$R_{\text{DCPD}} = k_1[\text{DCPD}] + k_i[\text{DCPD}]^{1/2} \quad (5)$$

The integrated form of eq 5 is difficult to use for a single kinetic run, but the series of runs of Table I is easily fitted by rearranging eq 5 to

$$\frac{[\text{DCPD}]^{1/2}}{R_{\text{DCPD}}} = \frac{1}{k_i} - a\frac{[\text{DCPD}]}{R_{\text{DCPD}}} \quad (6)$$

where $a = k_1/k_i$. The five gasometric runs of Table I give a linear plot of $[\text{DCPD}]^{1/2}/R_{\text{DCPD}}$ vs. $[\text{DCPD}]/R$, with the point corresponding to run 77 somewhat off. By least squares, this line has a slope of -0.29 and an intercept of 7300 with an index of determination of 0.966. If the point of run 77 is "smoothed"[10] to give an apparent first-order rate constant of 6.15×10^{-5} sec^{-1}, the least-squares index of determination rises to 0.996. For the slope and intercept of the unsmoothed plot, $k_1 = 4.0 \times 10^{-5}$ sec^{-1} and $k_2/k_3^{1/2} = 2.18 \times 10^{-2}$ $(M$ sec$)^{-1/2}$. For the smoothed plot, $k_1 = 3.9 \times 10^{-5}$ sec^{-1} and $k_2/k_3^{1/2} = 2.22 \times 10^{-2}$ $(M$ sec$)^{-1/2}$. The titrimetric runs seem to define another line of nearly equal slope, -0.27, but different intercept, 6150, so that $k_1 = 4.4 \times 10^{-5}$ sec^{-1} and $k_2/k_3^{1/2} = 2.5 \times 10^{-2}$ $(M$ sec$)^{-1/2}$. The index of determination for the three points is 0.994. There appears to be a small but real difference in the gasometric and titrimetric rates, and its origin is not clear. The total yield of carbon dioxide seems to exceed the theoretical for the first two runs, 68 and 77, but lags behind by *ca.* 0.04–0.05 mmol in the higher concentrations runs 74, 60, and 74. It may be that some trace impurity in the benzene solvent scavenges the alkoxy carboxyl radicals (by addition) and reduces the carbon dioxide yield.

With the value of a of eq 6 now determined, the integrated form[9] of eq 5

$$\ln\left(\frac{a + [\text{DCPD}]^{1/2}}{[\text{DCPD}]^{1/2}}\right) - \ln\left(\frac{a + [\text{DCPD}]_0^{1/2}}{[\text{DCPD}]_0^{1/2}}\right) = \frac{k_1 t}{2} \quad (7)$$

can be tested for single runs. A plot of

$$\ln\left[\frac{a + [\text{DCPD}]^{1/2}}{[\text{DCPD}]^{1/2}}\right] vs. \ t$$

was made with the points of run 74. A straight line to 28 ksec (82% decomposition) was obtained with a slope of 2.1×10^{-5} sec^{-1}, giving a value of 4.2×10^{-5} sec^{-1} for k_1, in good agreement with the other calculation. Use of the titrimetric value of a (0.27) on points of run 109 also gave a straight line corresponding to $k_1 = 5.0 \times 10^{-5}$ sec^{-1}, probably within experimental error of the value from the other analysis.

The chain length of the reaction, taken to be the ratio of DCPD decomposed by eq 2 (and 2b) to the DCPD decomposed by eq 1, is

(10) E. B. Wilson, "An Introduction to Scientific Research," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, p 215.

TABLE II

PRODUCTS OF DECOMPOSITION OF DICYCLOHEXYL PEROXYDICARBONATE

Run	Solvent	Initial DCPD concn, M	DCPD decompn,[a] mmol	Products, mmol		
				c-$C_6H_{11}OH$	c-$C_6H_{10}(O)$	Other
133	PhH	0.244	1.25	1.32	0.52	0.73[b]
136	PhH	0.0483	0.193	0.197	0.167	c
87	PhMe	0.0519	0.52	0.90	0.08	0.30 $(PhCH_2—)_2$
90	PhC(CH₃)=CH₂	0.0445	0.90	0.66	0.00	d
80	c-C_6H_{12}	0.492	1.00	1.52	0.05	e

[a] 95% or more of the starting DCPD. [b] 73 mg, nonvolatile at 100° and 0.1 Torr, and analyzing for $C_{6.00}H_{8.78}O_{1.34}$. [c] Nonvolatile not determined. [d] *Ca.* 100 mg of unidentified volatile products and 507 mg of nonvolatile material. [e] *Ca.* 25 mg each of two unidentified volatile products plus *ca.* 2 mg of another.

TABLE III

PRODUCTS OF DECOMPOSITION OF OO-t-BUTYL O-CYCLOHEXYL PEROXYCARBONATE AT 110°[a]

Run	Time, min	Solvent	Initial CBMP, mmol	Final CBMP, mmol	CO_2	c-$C_6H_{11}OH$	c-$C_6H_{10}(O)$	t-BuOH	AcMe	Other
117	1230	PhH	0.75	0.004	0.70	0.35	0.16	0.53	0.28	0.17 PhCH₃ 0.28[b] 0.007 PhPh 0.02 CO 0.14 CH₄
123	1312	PhC(CH₃):CH₂	0.86	0.017	~0.03	0.03		0.23	0.07	1.06[c]
125	1426	PhCH₃	1.10	0.007	d	0.87	0.12	0.98	e	0.61 $(PhCH_2—)_2$

[a] All solutions 0.14 to 0.16 M initially; 6 to 8 ml placed in sealed tubes. [b] 50 mg of nonvolatile residue, assumed mol wt 178, analyzing for $C_{12}H_{1.67}O_{1.72}$. [c] 567 mg of nonvolatile material; assumed average mol wt 534, analyzing for $C_{36.5}H_{46.2}O_{3.00}$. [d] CO_2 not quantitatively determined; some $-190°$ noncondensable, assumed to be methane, also found. [e] A spuriously high 0.58 mmol found; see discussion in text.

Thus, at DCPD concentrations of *ca.* 0.1 in benzene, the chain length is near unity and the amounts of DCPD decomposing by the two routes are about equal.

The products from complete decomposition of DCPD in benzene are cyclohexanol, cyclohexanone, and some resinous material that may arise from further reaction of cyclohexanone. The ratio of alcohol to ketone is 2.5 or 3.0:1 instead of the expected 1:1. The total yields of cyclohexanol and cyclohexanone seem to be nearly independent of the starting DCPD concentration (74 and 68% for 0.24 and 0.048 M DCPD). Biphenyl, specifically looked for, is not present in the product solutions at concentrations found by thermal conductivity glpc detectors. Although Razuvaev asserts that alkoxycarboxyl radicals decarboxylate, "resulting in the formation of RO· radicals,"[5d] we see no reason to make this assumption from the available data obtained at 50°. Abstraction of a hydrogen by the alkoxycarboxyl radical leads to a monoester of carbonic acid, expected to be in rapid equilibrium with the alcohol and carbon dioxide (eq 2a). Thus, the alcohol and carbon dioxide are products whether decarboxylation precedes hydrogen abstraction or not. Further, no simple cleavage products of cyclohexyloxy radicals (such as hexanal, hexenal, pentane, or pentene) are found. The greatly reduced yield of carbon dioxide when decompositions are done in solvents that scavenge by addition (styrene and α-methylstyrene; see below) also suggests that decarboxylation of cyclohexyloxycarboxyl radical is slow relative to competing bimolecular reactions. Also, the absence of the radical coupling product dicyclohexyl monopercarbonate is in accord with the postulate of no free alkoxy radicals being present. The monopercarbonate would be expected to be stable at 50° (see below).

Product and rate phenomena for decomposition of DCPD in other solvents are at least in qualitative accord with the preceding mechanism. In cyclohexane, the alcohol and ketone correspond to the carbon dioxide evolved. Consequently the unidentified products must contain the rest of the carbon dioxide in structures such as dicyclohexyl carbonate. The rate of decomposition of DCPD is approximately the same as in benzene, so it appears that cyclohexyl radicals may participate in the induced decomposition mechanism, although the low yield of cyclohexanone argues against this.

In α-methylstyrene and toluene, the rate of DCPD decomposition is reduced. The inert radicals formed by reaction of alkoxycarboxyl radicals with solvent, in one case by addition and the other by abstraction, apparently are not effective in promoting the induced decomposition of DCPD. For the α-methylstyrene decomposition (run 113, Table I), the apparent first-order rate constant, k_a, has a value of 5.9×10^{-5} sec^{-1} compared to the derived value of k_1, the true first-order rate constant for homolysis, of 4.4×10^{-5} sec^{-1}. The initial rate of decomposition in toluene solvent is anomalously low. The yield of bibenzyl from the decomposition in toluene suggests a minimum efficiency of radical production of 58%.

In α-methylstyrene, the carbon dioxide is only 29% of the theoretical value (run 90, Table I). Apparently, 71% of the I radicals added to the double bonds. Since the yield of cyclohexanol corresponds roughly to the carbon dioxide yield, most or all of the remaining 29% of I radicals may have abstracted allylic (methyl) hydrogens in the methylstyrene. A still greater reduction in carbon dioxide yield when

DCPD was decomposed in styrene has been reported;[11] the difference is thought to result from the absence of allylic hydrogen atoms in styrene.

OO-t-Butyl O-Cyclohexyl Peroxydicarbonate Decomposition.

—The early results of Strain on the decomposition of neat diisopropyl peroxycarbonate at 100°, where acetaldehyde was reported among the products,[3] suggested that the decarboxylation could be promoted by higher temperature. Consequently, the decomposition of CBMP at 110° was briefly investigated. If the stability of CBMP is similar to OO-t-butyl O-isopropyl peroxycarbonate,[12] its half-life is 3 hr at 110°. Thus CBMP should provide a smooth source of cyclohexyloxycarboxyl radicals (and t-butoxy radicals) at 110°.

Our results are summarized in Table III, where the products from the decomposition of CBMP in three solvents are reported. Evidence for the formation of cyclohexyloxy radicals would be the detection of fragmentation products, perhaps following the scheme
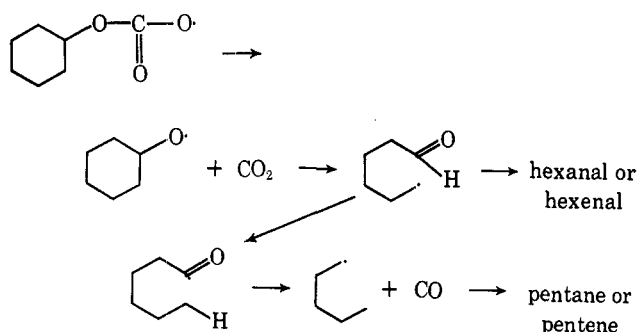
In the decomposition in benzene (run 117), where carbon dioxide loss and alkoxy fragmentation should have the best chance, there is a shortage of cyclohexyl groups of 0.24 mmol. There were no volatile products having the glpc retention time of hexanal, and the low yield of carbon monoxide renders the further degradation scheme unlikely. The best accounting for the missing cyclohexyl groups, as in the case of DCPD at 50°, seems to be in the small amount (0.28 mmol) of nonvolatile residue, bp >80° (0.1 Torr), found on distillation of the product mix. A molecular weight for the residue corresponding to one cyclohexyloxy and one benzene was taken for the calculations. Gray, Rathbone, and Williams formed cyclohexyloxy radicals by decomposing cyclohexyl nitrite in chlorobenzene at 100° and found about 50% of the expected cyclohexyl groups as cyclohexanol.[13] The fate of the remaining cyclohexyloxy groups was not determined, but since they report no other volatile products, it might be assumed that reaction of the radicals with solvent led to nonvolatile products. However, our residue could also arise from further attack on cyclohexanol and cyclohexanone and might not be related to existence of cyclohexyloxy radicals in solution.

The fragmentation of the concomitantly formed t-butoxy radical (whether the CBMP decomposition involves a chain mechanism or not) leads to a t-butyl alcohol–acetone ratio of 1.9. The ratio where t-butyl peroxide is decomposed in benzene,[14] is 0.28. It there-

fore appears that in the CBMP decomposition the reactant (or the cyclohexanol and cyclohexanone products) acted as a hydrogen donor and considerably raised the t-butyl alcohol yield.

In our experiment, the t-butyl alcohol and acetone account well for the total t-butoxy radical expected and the methane and toluene account for the methyl radicals that were lost when acetone was formed. A small amount of biphenyl is also detected.

The CBMP decomposition in α-methylstyrene (run 123) gave a very low yield of carbon dioxide, which suggests that the decarboxylation of the cyclohexylcarboxyl radical is still slow at 110° compared to its being scavenged by vinyl monomer. Yields of volatile products are low, and most of the CMBP fragments appear in combination with α-methylstyrene as nonvolatile product. The residue plus the volatile products account fairly well for all the oxygen in the starting CBMP.

Decomposition of CBMP in toluene gives cyclohexanol and cyclohexanone, which account for 91% of the expected cyclohexyl groups. Thus, decarboxylation to and subsequent fragmentation of the cyclohexyloxy group seems to be a minor reaction in the solvent. The bibenzyl yield indicates a minimum radical generation efficiency of 56%, similar to DCPD in toluene at 50°. The acetone yield was found to be an anomalously high 0.58 mmol, thus overaccounting for the t-butoxyl groups in the starting CBMP. If spurious contamination of our solution by acetone is assumed, 0.19 mmol of acetone, the amount predicted by Brook's acetone–t-butyl alcohol ratio from the decomposition of t-butyl peroxide in toluene,[15] makes a good t-butyl group balance.

Bartlett and Sakurai decomposed di-t-butyl monopercarbonate in cumene at 100° and determined the products formed.[16] In principle, one could determine the number of t-butoxy radicals formed (between one and two for each percarbonate decomposed) from the t-butanol–acetone ratio and the known[17] abstraction–cleavage competition that occurs when cumene is used as solvent at 100°. However, acetone is formed in small yield, and small (absolute) uncertainties in its determination lead to large uncertainties in the t-butyl alcohol–acetone ratio. The available data seem to be consistent with at least some decarboxylation of t-butoxycarboxyl radical before abstraction from solvent.

A final question to be asked is why the loss of carbon dioxide from alkoxycarboxyl radicals competes so poorly with bimolecular scavenging reactions while, evidently, alkylcarboxyl radicals cannot be trapped[18] or only inefficiently so.[19] The question is at least partly answered by the thermochemical parameters of the two reactions. The loss of carbon dioxide from acetoxy radicals is calculated[20] to be 20 kcal exothermic when the somewhat (±10 kcal) uncertain heat of formation of acetyl peroxide is used. Calculation of the value with the presently most reliable bond dissociation en-

(11) G. A. Razuvaev, L. M. Terman, and D. M. Yanovskii, *Dokl. Akad. Nauk SSSR*, **161**, 614 (1965).

(12) W. A. Strong, *Ind. Eng. Chem., Prod. Res. Develop.*, **3** (4), 264 (1964).

(13) P. Gray, P. Rathbone, and A. Williams, *J. Chem. Soc.*, 2620 (1961).

(14) J. H. T. Brook and W. Snedden, *Tetrahedron*, **20**, 1043 (1964).

(15) J. H. T. Brook, *Trans. Faraday Soc.*, **53**, 372 (1957).

(16) P. D. Bartlett and H. Sakurai, *J. Amer. Chem. Soc.*, **84**, 3269 (1962).

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(18) A. Rembaum and M. Szwarc, *J. Amer. Chem. Soc.*, **77**, 3486 (1955).

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ergy data[21] leads to an exothermicity of 11 kcal/mol. A similar calculation indicates that decarboxylation of the alkoxycarboxyl radical is slightly endothermic.[22]

$$RC(=O)—O· \longrightarrow R· + CO_2 \qquad \Delta H = -11 \text{ kcal}$$

$$ROC(=O)—O· \longrightarrow RO. + CO_2 \qquad \Delta H = 2 \text{ kcal}$$

The calculation is based on heats of formation of the hypothetical ROC(O)OH by group additivity rules[23] and the assumption that the hydrogen–oxygen bond dissociation energy of ROC(O)O–H is 107 kcal/mol, identical with carboxylic acids. That the decarboxylation has a substantial energy of activation is suggested by the low CO_2 yield from decompositions in styrene and α-methylstyrene. If it is assumed, as an upper limit, that *ca.* 10% of the radicals decarboxylate at 110° in α-methylstyrene and that an energy of activation of *ca.* 5 kcal attends the alkoxycarboxyl addition,[24]

(21) S. W. Benson, private communication. The heats of formation and bond dissociation energies necessary for the calculation are the same as listed in ref 18, with the exception that the O–H bond dissociation energy in CH₃COO–H has been revised to 107 kcal/mol.

(22) The author is indebted to Dr. D. M. Golden of Stanford Research Institute for this calculation.

(23) S. W. Benson, "Methods for the Estimation of Thermochemical Data," John Wiley & Sons, Inc., New York, N. Y., 1968, p 23.

(24) J. C. Bevington and J. Toole, *J. Polymer Sci.*, **28**, 413 (1958), choose 7 kcal as the activation energy for benzoyloxy addition to styrene. Their

then the decarboxylation reaction apparently has an activation energy of at least 20 kcal/mol. This is in contrast to the benzoyloxy radical, which was estimated[24] to decarboxylate with an activation energy of 14 kcal/mol. Calculation[23] of the thermochemistry of the decarboxylation of benzoyloxy indicates that it is also slightly endothermic by 1–3 kcal/mol. The decarboxylation of the acetoxy radical requires an estimated[25] 7.5-kcal/mol activation energy.

The high energy of activation associated with the decarboxylation of alkoxycarboxyl radicals and the reverse reaction may have interesting implications for other systems. For example, when di-*t*-butyl peroxyoxylate is decomposed in viscous solvents[26] at 45° and *t*-butoxy radicals are held in a solvent cage with carbon dioxide, addition of the *t*-butoxy to carbon dioxide (at the carbon atom) does not occur and the cage recombination product is di-*t*-butyl peroxide rather than di-*t*-butyl monopercarbonate. The percarbonate would be indefinitely stable at the 45° reaction temperature,[16] and should persist if formed.

Registry No.—I, R = *c*-C₆H₁₁, 1561-49-5; II, R = *t*-C₄H₉, R' = *c*-C₆H₁₁, 21690-93-7.

results also indicate a ratio of *A*'s of 10⁴ for decarboxylation *vs.* addition to styrene for benzoyloxy radical. This ratio was used in the α-methylstyrene calculation above.

(25) J. C. Martin, private communication.

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Acylketene Aminals

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New 3-unsubstituted isoxazolium salts were prepared by S$_N$1 alkylation, and an improved method was found to prepare 4-phenylisoxazole and achieve N-alkylation in one step. New stable acylketenimines were isolated from ring-opening of the isoxazolium salts, including the first stable acylketenimines without bulky, branched substituents on nitrogen. Primary and secondary amines were found to combine efficiently with acylketenimines to give acylketene aminals. The ketoketenimines from 4-methyl-5-phenylisoxazolium salts gave, instead, the tautomeric acylamidines.

Isoxazolium salts with hydrogen in the 3 position (**1**) have been shown to undergo spontaneous reaction with bases to give intermediate acylketenimines (**2**) (eq 1) which are consumed by addition of the conjugate acid of the starting base.[2,3] The reaction with an amine, aniline, was reported in one case, with the

N-ethylbenzisoxazolium cation (**3**) to give "a strongly basic substance," presumably the amidine **4** (eq 2).[3] In the present study it has been found that free primary and secondary amines themselves, in the absence of the conjugate acid ions, combine with acylketenimines in an efficient reaction to give acylketene aminals (**5**).

$$[—COC=C=N—] + BH \longrightarrow$$
$$\mathbf{2}$$

$$—COC(=C(B)—NH— \rightleftharpoons —COCH—C(B)=N— \qquad (1)$$

$$\mathbf{3}$$
$$\qquad (2)$$
$$\mathbf{4}$$

$$\mathbf{2} + H—N— \longrightarrow —COC=C—NH— \qquad (3)$$
$$\mathbf{5}$$

(1) National Science Foundation Graduate Trainee, 1966–1969.

(2) R. B. Woodward and R. A. Olofson, *J. Amer. Chem. Soc.*, **83**, 1007 (1961); *Tetrahedron Suppl.*, **7**, 415 (1966).

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