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Supercritical Carbon Dioxide. 5.[1] Carboxyinversion Reactions of Diacyl Peroxides. Alkyl Group Rearrangement and CO_2 Exchange

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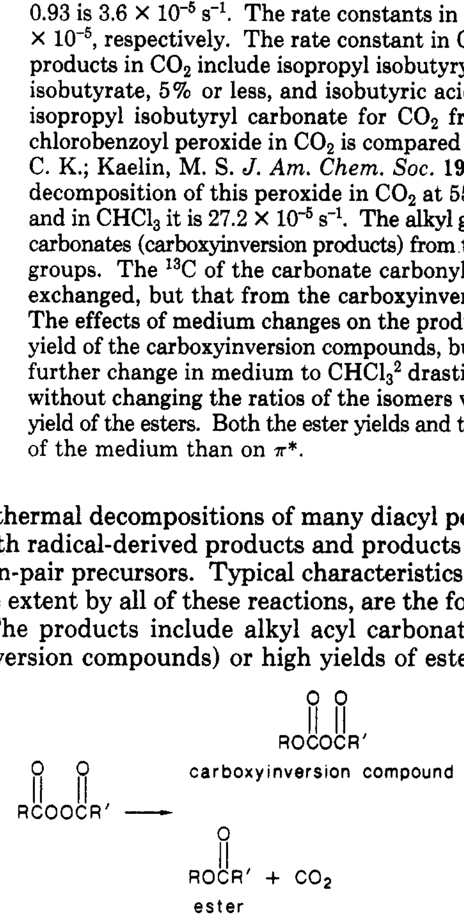
The decomposition of bis(isobutyryl) peroxide in supercritical CO_2, CCl_4, and $CHCl_3$ gives both radical and ion pair-derived products in all three media. The rate constant in supercritical CO_2 at 40 °C, π^* −0.05, and density 0.93 is 3.6×10^{-5} s^{-1}. The rate constants in CCl_4 and in $CHCl_3$ at the same temperature are 7.72×10^{-5} and 42.5×10^{-5}, respectively. The rate constant in CO_2 fits a relationship with π^* observed for aromatic solvents.[5] The products in CO_2 include isopropyl isobutyryl carbonate (the carboxyinversion compound), 17% yield, isopropyl isobutyrate, 5% or less, and isobutyric acid, 17% yield. There is no exchange of the inverted CO_2 moiety of isopropyl isobutyryl carbonate for CO_2 from the medium. The decomposition of cyclobutanecarbonyl *m*-chlorobenzoyl peroxide in CO_2 is compared with the results reported by Taylor et al.[2] (Taylor, K. G.; Govindan, C. K.; Kaelin, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2091) in conventional solvents. The rate constant for the decomposition of this peroxide in CO_2 at 55 °C at a density of 0.81 is 2.2×10^{-5} s^{-1}, in CCl_4 it is 2.93×10^{-5} s^{-1}, and in $CHCl_3$ it is 27.2×10^{-5} s^{-1}. The alkyl groups in the alkyl *m*-chlorobenzoate esters and alkyl *m*-chlorobenzoyl carbonates (carboxyinversion products) from this peroxide are rearranged in part to cyclopropylmethyl and 3-butenyl groups. The ^{13}C of the carbonate carbonyl in the cyclopropylmethyl *m*-chlorobenzyl carbonate is about 12% exchanged, but that from the carboxyinversion product with the unrearranged alkyl group is not exchanged. The effects of medium changes on the product are as follows: the change from CO_2 to CCl_4[2] increased the total yield of the carboxyinversion compounds, but did not change the relative yields of the isomers appreciably. The further change in medium to $CHCl_3$[2] drastically lowered the total yield of carboxyinversion compounds, again without changing the ratios of the isomers very much, and at the same time caused a large increase in the total yield of the esters. Both the ester yields and the rate appear to depend more on the hydrogen-bond-donor properties of the medium than on π^*.

The thermal decompositions of many diacyl peroxides give both radical-derived products and products derived from ion-pair precursors. Typical characteristics, shared to some extent by all of these reactions, are the following:

(1) The products include alkyl acyl carbonates (carboxyinversion compounds) or high yields of esters.



(2) Polar solvents or appropriate substituents increase both the rate and the proportion of products derived from ion pairs.

(3) The rate of production of radicals increases along with the rate of production of ion pairs, though not to the same extent.

Rearrangements within the Alkyl Group. Cyclobutanecarbonyl *m*-chlorobenzoyl peroxide (P_{cb}) and two isomers P_{cpm} and P_{bte}, in which the alkyl groups[3] are cyclobutyl, cyclopropylmethyl, and 3-butenyl, respectively, have been studied by Taylor et al.[2] The same subscripts will be used to designate the structures of the alkyl groups in products.

The decomposition of P_{cb} and P_{cpm} in CCl_4 and in $CHCl_3$ gave *m*-chlorobenzoic acid, the alkyl *m*-chlorobenzoyl carbonates (carboxyinversion compounds) C_{cb},[3] C_{cpm}, and C_{bte}, and alkyl *m*-chlorobenzoate esters E_{cb}, E_{cpm}, and E_{bte}, in which the original alkyl group had been partially isomerized to give the other two structures. P_{bte} gave mainly radicals, the acid, the three esters, and C. In the C isomers from P_{cb} and P_{cpm} the major product retained the structure from the original peroxide. But E_{cpm} was the major component of the esters from all three peroxides. The decomposition in acetonitrile gave a mixture of *N*-acetyl-*N*-*m*-chlorobenzoyl alkylamines, the major product again being the one with the cyclopropylmethyl group.

To explain the internal rearrangement of the migrating group in the carboxyinversion reaction, Taylor proposed a mechanism in which an intermediate ion pair loses CO_2 *reversibly*, which means that exchange of CO_2 with the medium should occur in supercritical carbon dioxide.

Isobutyryl Peroxide. The decomposition of bis(isobutyryl) peroxide (P_{ip}) has been studied in a number of conventional solvents of different polarities.[4,5] The products included scavengeable radicals, the carboxyinversion compound C_{ip}, isopropyl isobutyrate (E_{ip}), and hydrocarbons. In acetonitrile, a nucleophilic reaction of that solvent with an ion pair trapped some of the isopropyl groups, recovered on workup as *N*-isopropylacetamide.[4]

Increasing the polarity of the solvent increased both the decomposition rate and the proportion of polar product, but the product continued to include scavengeable radicals even in acetonitrile.[4] The relation between the rate constant and the polarity of the solvent depends on the solvent type. A plot of $\log_{10} k$ for benzene, nitrobenzene, benzo-

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[2] Taylor, K. G.; Govindan, C. K.; Kaelin, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2091.

[3] The following conventions have been used for structures: subscripted P, C, and E are peroxides, alkyl acyl carbonates (carboxyinversion compounds), and esters, respectively. Subscripts indicate the structure of the alkyl group. P_{ip} is bis(isobutyryl) peroxide. P_{cb}, P_{cpm}, and P_{bte} are cyclobutyl, cyclopropylmethyl, and 3-butenyl *m*-chlorobenzoyl peroxides. Subscripts cb, cpm, and bte indicate that the alkyl group is cyclobutyl, cyclopropylmethyl, or 3-butenyl, respectively. C_{ip} is isopropyl isobutyryl carbonate. E_{ip} is isopropyl isobutyrate. C_{cb}, C_{cpm}, and C_{bte} are the corresponding alkyl *m*-chlorobenzoyl carbonates (carboxyinversion compounds). E_{cb}, E_{cpm}, and E_{bte} are the corresponding alkyl *m*-chlorobenzoates.

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Table I. Peroxide Decomposition Rates

peroxide[3]	solv	π^*[6]	temp, °C	$10^5 k$, s^{-1}	conditions
P_{ib}	CO_2	ca. −0.05[1a]	40	3.58 ± 0.47	density 0.93 g/mL
	CCl_4	0.28	40	7.72 ± 0.11[16]	C_0 0.026 M
			40	7.85 ± 0.02[5]	
	$CHCl_3$	0.58	40	42.5 ± 0.5	C_0 0.035 M
P_{cb}[c]	CO_2	ca. −0.15[1a]	55	2.17 ± 0.32[b]	density 0.81[a] g/mL, C_0 0.02[a] M
	CCl_4	0.28	55	2.93 ± 0.07	C_0 0.04 M
	$CHCl_3$	0.58	55	27.2 ± 0.15	C_0 0.04 M

[a] Mean values, from product runs. [b] In most runs the reaction was quenched during the second half-life. [c] For comparison, the rate constant for bis(cyclobutanecarbonyl) peroxide in CCl_4 at 55 °C is 1.68×10^{-5}.[7]

nitrile, chlorobenzene, toluene, *p*-xylene, CCl_4, and cyclohexane shows a good correlation with the Kamlet–Taft[6] π^* parameter (eq 1). Points for other kinds of solvent, namely 2-propanol, fluorobenzene, acetonitrile, and $CHCl_3$[15] deviate significantly.

$$\log_{10} k = -4.370 + 1.078\pi^* \qquad (r = 0.973) \qquad (1)$$

The fact that the points for CCl_4 and cyclohexane fit eq 1 just as well as those for the aromatic solvents means that the ∂ polarizability correction is unimportant for this reaction.[6]

Results

Kinetics. Rate constants for the decomposition of isobutyryl peroxide (P_{ip}) and cyclobutanecarbonyl *m*-chlorobenzoyl peroxide P_{cb} in supercritical CO_2, CCl_4, and $CHCl_3$ are given in Table I.

The inclusion of the rate constant for P_{ip} in CO_2 in the set of solvents correlated (eq 1) with the Kamlet–Taft π^* parameters[6,1a] slightly improves *r* while changing the intercept and slope to −4.414 and 1.138, respectively. The rate constant for cyclobutanecarbonyl *m*-chlorobenzoyl peroxide in supercritical CO_2 at 55 °C was obtained from the product runs discussed below. Points from experiments with higher initial or higher mean peroxide concentrations had higher rates, indicating that there is some induced decomposition. No correlation with the density or π^* of the CO_2 was evident within the narrow range of densities and π^* used.

Products. Isobutyryl Peroxide. The decomposition of isobutyryl peroxide (P_{ip}) in CO_2 at 40 °C and a density of 0.81 g/mL gave a 17 mol % yield of the carboxyinversion product isopropyl isobutyryl carbonate (C_{ip}), less than 5% isopropyl isobutyrate (E_{ip}), and 17% isobutyric acid. The more volatile products, propane, propylene, and 2,3-dimethylbutane, were swept away during the venting of the reaction vessel and were not examined. The decomposition in cyclohexane at 40 °C went at about the same rate and gave about the same yields, 17.9% C_{ip} and 5.7% E_{ip}.[4]

Cyclobutanecarbonyl *m*-Chlorobenzoyl Peroxide (P_{cb}). The decomposition of cyclobutanecarbonyl *m*-chlorobenzoyl peroxide (P_{cb}) in CO_2 at 55 °C, densities 0.71–0.87 g/mL, and initial peroxide concentrations 0.01–0.027 M gave the isomeric carboxyinversion compounds C_{cb} and C_{cpm}, traces of C_{bte}, all three esters E_{cb}, E_{cpm}, and E_{bte}, *m*-chlorobenzoic acid, and small amounts of cyclobutanecarboxylic acid. The hydrocarbon products, most of which were lost in venting, were not investigated.

Table II. Cyclobutanecarbonyl *m*-Chlorobenzoyl Peroxide Products[a] in CO_2[c]

product	% yield[h]	product	% yield[h]	product	% yield[h]
C^{d}	48.3 ± 2.5	C_{cb}[f]	43.6 ± 2.3	E_{cb}[f]	5.4 ± 0.3
E^{d}	28.3 ± 1.7	C_{cpm}[f]	4.9 ± 0.3	E_{cpm}[f]	18.5 ± 1.1
acid[b,e]	29.9 ± 0.2	C_{bte}	trace	E_{bte}[f]	4.2 ± 0.6
	% of (C + E)		% of (C + E)		% of (C + E)
C^{g}	63.3 ± 1.5				
		C_{cb}[g]	56.9 ± 1.3	E_{cb}[g]	7.1 ± 0.3
		C_{cpm}[g]	6.4 ± 0.3	E_{cpm}[g]	24.2 ± 1.1
		C_{bte}[g]	trace	E_{bte}[g]	5.5 ± 0.8

[a] C is the total mol % yield of carboxyinversion compound $ROCOOCOC_6H_4Cl$. E is the total yield of ester $ROCOC_6H_4Cl$. Subscripts cb, cpm, and bte denote R = cyclobutyl, cyclopropylmethyl, and 3-butenyl. [b] Total yield of acids determined by titration, mainly *m*-chlorobenzoic acid. [c] In supercritical CO_2 at 55 °C, this paper. [d] From four runs at low peroxide concentrations. Mean peroxide concentrations 0.0026–0.0064 M, CO_2 densities 0.75–0.87 g/mL. [e] From two runs at low peroxide concentrations. [f] Calculated as mean fraction of C × %C or of E × %E. [g] From all eight runs. Mean peroxide concentrations 0.0026–0.019 M, CO_2 densities 0.71–0.87 g/mL. Unlike the total yields per mole of peroxide decomposed, the product ratios were not sensitive to the peroxide concentration or amount of induced decomposition. [h] Based on peroxide decomposed.

The product mixtures were analyzed for the carboxyinversion compounds, esters, total acids, and remaining peroxide at reaction times that left some of the peroxide undecomposed. This was done to minimize secondary reactions. The total yields of C_{cb} C_{cpm}, and the esters were highest and least erratic in runs in which the mean peroxide concentrations during the runs were lowest. These are the runs whose mean yields of total C and E are given in Table II. The probable reason for the behavior of the C and E yields at higher peroxide concentrations is radical-induced decomposition, an explanation that accounts for some of the rates as well. Taylor's total yields of C in CCl_4 and $CHCl_3$ also were lower in the more concentrated runs, but the yields of E_{cb} and E_{cpm} in CCl_4 increased.

In contrast to the total yield of C + E, the ratio C/E and the relative amounts of the isomeric C and E components (Table II) were nearly constant from run to run, independent of the peroxide concentration and the CO_2 density.

Carbon Dioxide Exchange

Isobutyryl peroxide and cyclobutanecarbonyl *m*-chlorobenzoyl peroxide labeled in the alkanoyl carbonyl(s) with ^{13}C were decomposed in supercritical CO_2 and the products examined for CO_2 exchange by GC–MS. The carboxyinversion products C_{ip} from P_{ib} and C_{cb}, the unrearranged isomer from P_{cb}, showed no exchange or less than 1%. It was not possible to obtain any useful result from the trace of C_{bte}. The label in C_{cpm} was 12% exchanged (Table III).

Discussion

Hypothesis of a Common Intermediate. The observation that polar solvents or appropriate substituents seem to increase the rate of formation not merely of ion pairs but also of radicals has led to the hypothesis of a common rate-determining step and a common intermediate for both types of product.[4,8] According to this hypothesis, the

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Table III. % $^{12}C/^{13}C$[a]

	P_{cb}	C_{cb}[d]	C_{cpm}[d]
	71.6[b] ± 6.5	73.6[e] ± 1.8	94.8[e] ± 5.9
	72.6[c]	73.8[f] ± 1.2	87.5[f] ± 6.4
		72.5[g] ± 1.8	90.6[g] ± 6.3
means	72.6	73.2[h] ± 1.8	89.1[h] ± 5.6
% exchange[h]		0.5	12

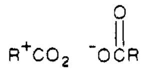
[a] By GC–MS–SIM(EI). The error limits are standard deviations of the intensities measured at a number of points across the GC peak. [b] From the molecular ion of the *N,N*-diethylcyclobutanoylamide made from peroxide remaining at the end of the run. [c] Nominal, calculated from the synthesis of the peroxide. [d] From the Et_2NCO^+ ion from the carbamate $ROCONEt_2$ GC peak. [e] Thermolysis conditions: 40 °C, density 0.81 g/mL, extent of reaction 59%. C_{cb}/C_{cpm} ratio 90/10. [f] Thermolysis conditions: 40 °C, density 0.86 g/mL, extent of reaction 73%. C_{cb}/C_{cpm} ratio 89/11. [g] Thermolysis conditions: 40 °C, density 0.75 g/mL, extent of reaction 75%. C_{cb}/C_{cpm} ratio 90/10. [h] Mean of all runs (*e*, *f*, and *g*).

competing product-determining steps branch from that intermediate rather than from the peroxide itself.

It is clear that the hypothesis of independent ionic and radical reactions, in which the ionic reaction is sensitive to polar solvents or substituents, and the radical reaction is almost completely *insensitive*, it will not accommodate the data from many diacyl peroxides. In the case of cyclobutanecarbonyl *m*-chlorobenzoyl peroxide, the increase in rate from CCl_4 to $CHCl_3$ seems to be accompanied by almost no change in the proportion of radical products, estimated[2] to be 5–10%. It is appropriate to note, however, that the apparent increase in the rate of production of radicals only requires a polar transition state, not necessarily a polar intermediate. The transition state of a radical-producing reaction might have the needed polar character if there is an ionic surface close enough in energy for configuration interaction.

Scheme I is an attempt to rationalize both our results for the thermolysis of P_{cb} in CO_2, our rates in CO_2, CCl_4, and $CHCl_3$, and Taylor's products from the reaction in CCl_4, $CHCl_3$, and CH_3CN. The network of product-determining paths could start either from the peroxide or from a hypothetical hybrid ion-pair/radical-pair first intermediate. This feature does not seem to be absolutely required by the evidence in the particular case of peroxide P_{cb}, although we have included it in Scheme I.

Exchange, Rearrangement, and CIDNP.[2] In the $^{13}CO_2$ exchange experiments the carboxyinversion product from isobutyryl peroxide and the carboxyinversion product C_{cb} from P_{cb} did not show any experimentally significant carboxyl exchange. In contrast, the isomer C_{cpm}, with rearranged alkyl group, showed about 12% exchange. The absence of exchange of CO_2 in C_{cb} and the presence of CO_2 exchange in C_{cpm} require that most of the C_{cb} be formed by a route that is separate and well insulated from any paths involving ion pairs such as (IP1) in which R_{cb}^+ is not bonded in some way to the CO_2.

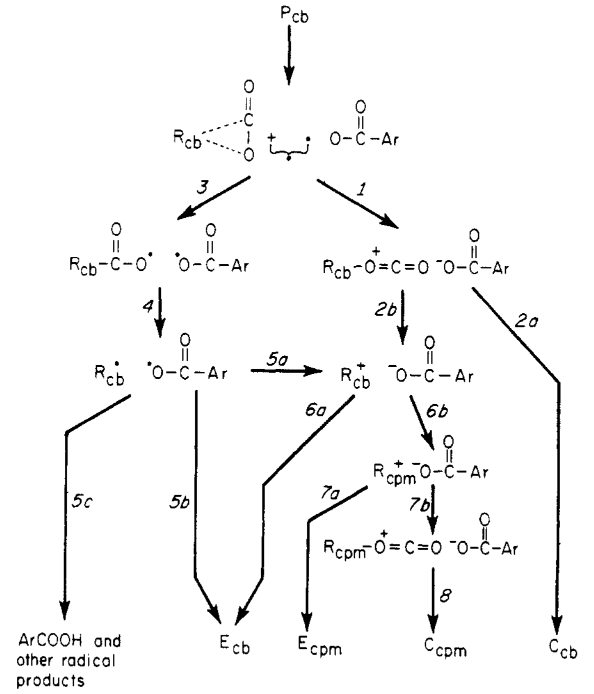


$$R^+CO_2\ \ {}^-O\overset{\overset{O}{\|}}{C}R'$$

IP1

The reason that C_{cb} is not formed from IP1 or a similar ion pair to a detectable extent is that the rearrangement of the cyclobutyl cation to the cyclopropylmethyl cation is irreversible and fast compared to the rebonding of R^+ with CO_2. The formation of ester E_{cb} is able to compete to a certain extent, but the major isomer is always E_{cpm}.

Scheme I



C_{cb} is 90% of the total C formed in CO_2 and 85% in CCl_4. Additional support for the existence of a path not involving unbonded alkyl cations is the behavior of P_{cb} in acetonitrile.[2] That nucleophilic solvent traps 49% of the alkyl groups, but still leaves a 10% yield of C, more than 96% of which is the unrearranged isomer C_{cb}.

Since the lifetime of R_{cpm}^+ is considerably longer than that of R_{cb}^+, it is possible for the former to recapture CO_2 and give carboxyl-exchanged C_{cpm}, which it does to the extent of about 12%. C_{bte} should also be exchanged, but was too minor a product for this to be detected.

The absence of a CIDNP signal from C_{cb} requires a path that is also reasonably well insulated from radical-pair intermediates. In Scheme I, path 1,2a meets both requirements.

A free radical branch of the reaction, path 3,4,5b, contributes to the formation of E_{cb}, which thus shows a moderate CIDNP signal.[2]

Since cyclobutyl radicals do not rearrange,[10] the rearranged esters must have ionic precursors. Some of these ionic precursors, but not a major portion, must have been formed by electron transfer in radical pairs, since a weak CIDNP signal was detected from E_{cpm}. Polarized C_{cpm} could also, in principle, be formed from radicals via the R_{cpm}^+ $-OOC-Ar$ ion pair. However, the signal from E_{cpm} was barely detectable,[2] and the amount of C_{cpm} formed by this route would be even less than the amount of E_{cpm}.

Medium Effects. The change in medium from CO_2 (π^* ca. −0.2) to CCl_4 (π^* +0.28) increased the rate of disappearance of P_{cb} by about a factor of 1.4. It also increased the yield of the carboxyinversion products C by about the same factor, from 48% in CO_2 to about 70% in CCl_4.[17] In

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(15) The rate constant given in ref 5 for $CHCl_3$, which was reported to be almost the same as that for the much less polar solvent CCl_4, is too low by about a factor of 5.

terms of Scheme I, the reason for the increase is an acceleration by the more polar solvent of steps 1 relative to step 3, and a decrease in wastage of the peroxide by radical–induced decomposition.

The same change in medium slightly *decreased* the yield of esters E from 28% in CO_2 to 21% in CCl_4. We attribute this to a relative slowing down of the radical paths 3,4,5 which also lead to ester. When the ester yields are broken down into E_{cb}, E_{cpm}, and E_{bte}, it is found that E_{cb} has decreased about 31%, from a 5.4% yield to a 3.7% yield, while the decrease in the sum of the E_{cpm} and E_{bte} yields was only 22%. This medium change is particularly unfavorable to E_{cb}, which, since the cyclobutyl radical does not rearrange, is the only ester formed by the important radical path 3,4,5b. The more polar medium may also have decreased formation of E_{cb} by nongeminate radical combination and by induced decomposition.

The further increase in polarity of the solvent from CCl_4 (π^* +0.28) to $CHCl_3$ (π^* +0.58, α 0.44) has a much larger effect than the change from CO_2 to CCl_4. The rate increased by an order of magnitude, and the relative importance of the total E and total C in the product is reversed. Since the ratios E_{cb}/E, E_{cpm}/E, C_{cb}/C, and C_{cpm}/C do not change very much, it is probable that the precursors of these isomeric products remain the same and also that nothing disturbs the ratios of the rate constants for R^+ rearrangement relative to the rate constants for ester formation. Since $CHCl_3$ is a hydrogen-bond donor (α = +0.44), it may acclerate a reaction like 2b, solvating the departing CO_2. This allows 2b to compete more successfully with 2a, in which hydrogen-bonded carboxylate anions would have to act as nucleophiles. The increase in yield of E is achieved mainly at the expense of C_{cb}.

Experimental Section

The CO_2 was Airco instrument grade, minimum purity 99.99%, max O_2 4 ppm, max N_2O 4 ppm, max total hydrocarbon 10 ppm, and max H_2O 10 ppm. Reactions were carried out in stainless steel high-pressure vessels fitted with removable glass liners. The glass liners had Teflon caps pierced by a 0.3-mm hole. A 10–15-mg sample was weighed into the liner, a glass bead was added for stirring, and the liner was placed in the bomb. Air was purged from the bomb by evacuating it and flushing with CO_2 at the supply cylinder pressure. Additional CO_2 was then pumped in[1a] until the desired density of CO_2 was reached. The bomb was then heated in a thermostated oil bath, and the initial and quenching times were noted. The reaction was quenched by immersing the bomb in ice–water, then the bomb was slowly vented to atmospheric pressure, allowed to come to room temperature, and opened, and the products were washed out with CH_2Cl_2.

Products from Cyclobutanecarbonyl *m*-Chlorobenzoyl Peroxide. After a known amount of methyl *o*-bromobenzoate was added, the product mixture was allowed to react with excess diethylamine for several hours. This treatment converts the isomeric carboxyinversion compounds C into the *N,N*-diethylurethanes[2] and *N,N*-diethyl-*m*-chlorobenzamide. The excess amine was extracted with 5% HCl, and the acids were either extracted with 10% aqueous $NaHCO_3$ or derivatized with diazomethane. The esters, urethanes, and amides were analyzed by GC on a 30-m, 0.25-mm i.d., capillary column bonded with Supelco Wax-10 poly(ethylene glycol), thickness 25 μm.

Control experiments with authentic samples of C_{cb} and C_{cpm}[2] showed that the yields of the corresponding urethanes were 44% for C_{cb} and 51% for C_{cpm}. These results were used to determine the yields of the isomeric carboxyinversion products.

Cyclobutanecarbonyl *m*-Chlorobenzoyl Peroxide. The unlabeled peroxide was made from the acid chloride and *m*-chloroperbenzoic acid.[2] [^{13}C]Carbon dioxide from $BaCO_3$, 91.8% ^{13}C, was used to make the labeled acid from cyclobutyl Grignard reagent. The labeled acid was diluted with a known amount of unlabeled acid, and this mixture used to make peroxide P_{cb} by the cyclohexylcarbodiimide method.[11]

Isobutyryl Peroxide. Isobutyryl peroxide was made by the method of Greene and Kazan.[11] Products from the thermolysis in CO_2 were analyzed by infrared spectroscopy and by converting the carboxyinversion product into the urethane and amide with diethylamine. The ^{13}C-labeled peroxide was made in the same way as the cyclobutanecarbonyl *m*-chlorobenzoyl peroxide.

Carbon Dioxide Exchange. The products from the decomposition of the labeled cyclobutanecarbonyl *m*-chlorobenzoyl peroxide were analyzed for $^{13}C/^{12}C$ isotopic ratios by GC–MS using selected ion monitoring (SIMS) with electron-impact ionization. The results from a set of scans of the selected ion across the top of the GC peak were averaged.[12–14]

The carboxyinversion product from the decomposition of isobutyryl peroxide was stable enough to survive the GC column, and chemical ionization gave strong molecular ion peaks. The amount of exchange was calculated from the ratio of ions with two labels to ions with one label, integrating over the entire peak. The value of the ratio from a solid-probe mass spectrum of the acid used in the synthesis of the peroxide was used as a control.

Acknowledgment. We thank the National Science Foundation for support of this work under Grant CHE-8217287.

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(16) This paper.

(17) Figures cited in comparing products from our runs at 55 °C with those in conventional solvents (ref 2) are the mean of yields in the more dilute runs in those solvents at 40 and 60 °C.