Decomposition of Diacyl Peroxides. Part 9. Mechanism of the Carboxy-inversion Process in the Thermal Decomposition of Benzoyl Cyclohexanecarbonyl Peroxide and Related Diacyl Peroxides

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Mechanisms of the carboxy-inversion process in the thermal decomposition of benzoyl cyclohexanecarbonyl peroxide and related diacyl peroxides have been investigated in detail by elabolate ^{18}O-tracer experiments which involve measurements of ^{18}O-scrambling of benzoyl cyclohexyl carbonate resulting from the initial carboxy-inversion process under the reaction conditions. A detailed analysis of the ^{18}O-tracer experimental results reveals that the carboxy-inversion process of Case I and II peroxides involves three kinds of ion pairs. The extents of the contribution of these ion pairs in the carboxy-inversion process of benzoyl cyclohexanecarbonyl peroxide and *m*-chlorobenzoyl cyclohexanecarbonyl peroxide have been determined. Details of the mechanisms of the thermal decomposition of diacyl peroxides have been discussed based on the ^{18}O-tracer, kinetic, product-distribution and CIDNP experimental results and solvent effects on the decomposition.

Leffler[1,2] found that decomposition of *p*-methoxybenzoyl *p*-nitrobenzoyl peroxide (**1**), a highly polarized peroxide, is converted, mainly through the ionic carboxy-inversion process, into *p*-methoxyphenyl *p*-nitrobenzoyl carbonate (**2**). The carboxy-inversion process has since been revealed to be very important in the thermal decomposition of symmetrical aliphatic diacyl peroxides.[3–16] The following observations seem to demonstrate the ionic nature of the reaction. (*a*) The carboxy-inversion process is accelerated in polar media[1,4,5,10,14] and is catalysed by both Brönsted and Lewis acids.[1,11,17–19] (*b*) The configuration of the migrating alkyl group is maintained throughout the inversion process.[4,9,19] (*c*) The rate of the carboxy inversion increases as the ability of the migrating alkyl group to form the corresponding carbocation increases.[4,6,9,11,12] Similarly, the introduction of an electron-withdrawing substituent on the migrating carboxylate group also accelerates the reaction.[2,6,7] (*d*) The kinetics of the carboxy-inversion process gives a large negative activation volume[8] and lower activation enthalpy and activation entropy than the radical decomposition process.[5,7,9] (*e*) The migrating alkyl group rearranges specifically to the adjacent peroxidic oxygen atom.[9,12,13,19,20] Since, usually, thermolyses of these diacyl peroxides gives both radical-reaction and the carboxy-inversion products, the thermolysis of various diacyl peroxides appears to be a good system in which to investigate the nature of these dual processes, which arise from the same starting material. One interesting problem which has received a great deal of attention in recent years is how these dual processes of decomposition merge or deviate.[10,11,13–16,21]

Denney proposed the following intimate ion-pair mechanism (Scheme 1) for the carboxy-inversion of (**1**) on their ^{18}O-tracer experimental results; *i.e.* O-a of (**2**) obtained from α-oxygen ^{18}O-labelled peroxide did not contain any of the original ^{18}O-label. This was taken to mean that all the original ^{18}O-label was retained in O-b of (**2**), though there was no experimental evidence for the retention.[20] Since O-d of the inversion product (**2**) was found to have retained 66% of the original ^{18}O-label in the δ-^{18}O-labelled peroxide (**1**), the remaining 34% of the original ^{18}O-label was assumed to be located in O-c of (**2**).[22] However, when α-^{18}O-labelled 1-apocamphoryl benzoyl peroxide (**3**)α and δ-^{18}O-labelled 1-apocamphoryl benzoyl peroxide (**3**)δ were allowed to decompose in carbon tetrachloride, separately, both peroxides were found to give the inversion product, 1-apocamphyl benzoyl carbonate (**4**) of the same ^{18}O-distribution, in which the original ^{18}O-labels in both (**3**)α and (**3**)δ were found to be equilibrated into O-b, -c, and -d of the inversion product (**4**) [Scheme 2(*a*)].[12] ^{18}O-Scrambling was found to take place among O-b, -c, and -d of the inversion product to give (**4**)bcd in the control experiment, which was carried out separately with specifically O-c and -d ^{18}O-labelled 1-apocamphyl benzoyl carbonate (**4**)cd under the same conditions applied to the decomposition of the peroxide (**3**α and (**3**)δ [Scheme 2(*b*)]. The experimental observations shown in Scheme 2(*a*) have been interpreted by the following mechanistic scheme shown in Scheme 3.[12,23] However, one cannot rule out the possibility that the carboxy-inversion process of (**3**)α and (**3**)δ does not give specifically ^{18}O-labelled inversion products, (**4**)b and (**4**)d, respectively, but affords directly the inversion product (**4**)bcd with either partial or complete scrambling of the original ^{18}O-labels of the peroxides, since the occurrence of the ^{18}O-scrambling in the inversion product [Scheme 2(*b*)] obscures the ^{18}O-experimental evidence to support the carboxy-inversion mechanism.

Meanwhile, another type of ^{18}O-scrambling was found to take place in the thermal decomposition of diacyl peroxides as shown in Scheme 4.[24–29] This ^{18}O-scrambling also complicates the ^{18}O-tracer study of the carboxy-inversion mechanism. In an earlier study, we classified diacyl peroxides, R–C(O)O–O(O)C–R′, based on the structure of R and R′, *i.e.* case I peroxide: R,R′ = alkyl; case II peroxide: R = alkyl, R′ = aryl; case III peroxide: R,R′ = aryl, and correlated the structure of diacyl peroxides with the rate of the oxygen scrambling in diacyl peroxide (Scheme 4), k_{sp}, and the ester yield by radical processes, in which the rate (k_{sp}) of the ^{18}O-scrambling in Scheme 4 decreases in the order I > II > III.[28]

In order to elucidate the mechanism of the carboxy-inversion by ^{18}O- tracer experiments, one has to choose a suitable diacyl peroxide for which carboxy-inversion proceeds markedly faster than the ^{18}O-scrambling reactions in both the peroxide

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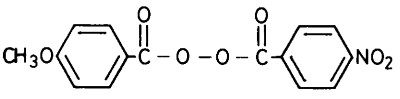

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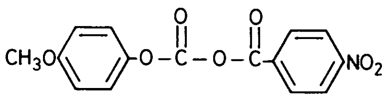

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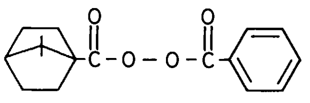

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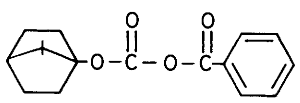

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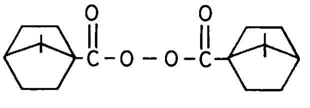

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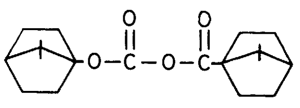

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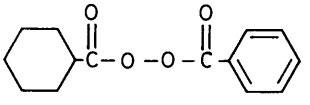

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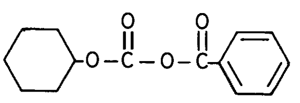

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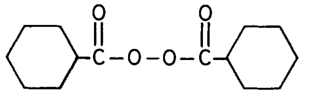

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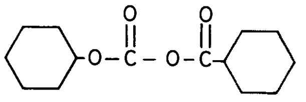

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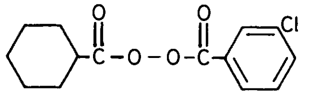

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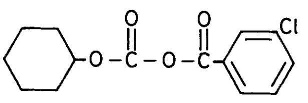

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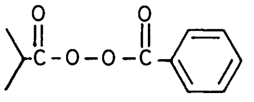

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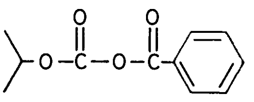

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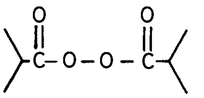

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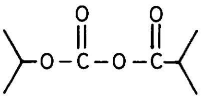

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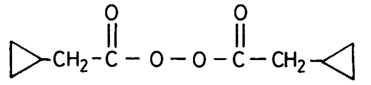

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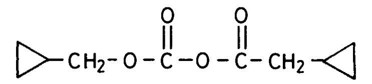
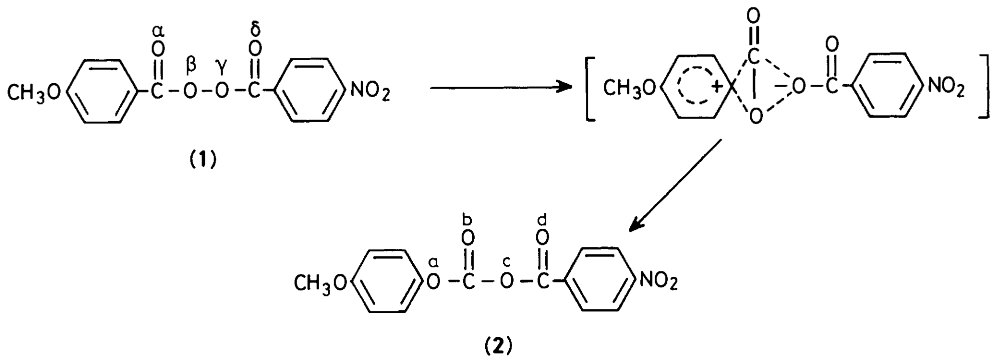
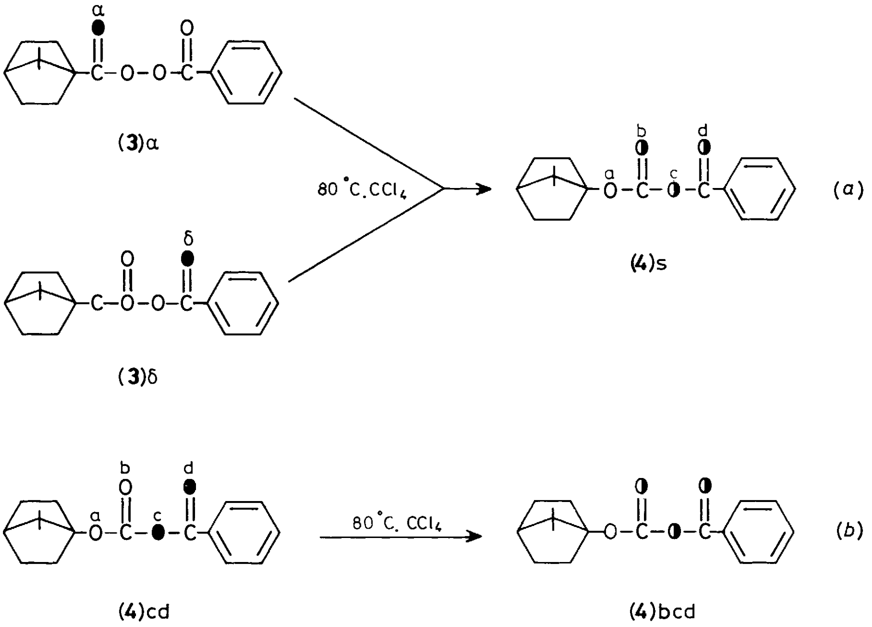


(18)

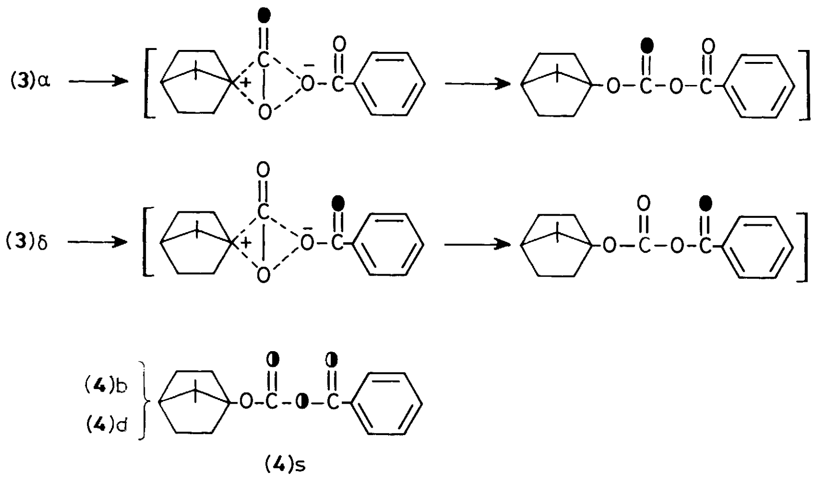
(Scheme 4) and the carboxy-inversion product [Scheme 2(*b*)]. We have noticed that the thermolysis of cyclohexyl benzoyl carbonate (**8**)cd labelled with ^{18}O specifically at O-c and -d in carbon tetrachloride is characterized as follows. (*a*) The oxygen scrambling takes place between O-b and -c oxygens at a moderate rate at 45 °C. (*b*) Practically no scrambling of O-d proceeds under the conditions; however, the scrambling among O-b, -c, and -d takes place at 75 °C. (*c*) O-a does not equilibrate with other oxygen atoms at all at elevated temperatures.[30] Bis(cyclohexanecarbonyl) peroxide (**9**) is known to decompose at a rate of 2.02×10^{-4} s^{-1} to give the inversion product, cyclohexyl cyclohexanecarbonyl carbonate (**10**) as a major product, while its oxygen scrambling between α and β oxygens (Scheme 4) proceeds very slowly compared with the decomposition, *i.e.* 2.00×10^{-6} s^{-1}.[31] The corresponding case II peroxide, *i.e.* benzoyl cyclohexanecarbonyl peroxide (**7**) is expected to decompose to afford the inversion product, cyclohexyl benzoyl carbonate (**8**) as a major product in a rate comparable to that of the decomposition of the corresponding case I peroxide, as we have already observed with 1-apocamphoryl peroxide (**5**) (case I peroxide) and the corresponding case II peroxide (**3**), both of which decompose at similar rates and afford the inversion products as major products. However, the ^{18}O-scrambling (Scheme 4) was markedly slower than that of the decomposition with the case II peroxide (**3**), while the ^{18}O-scrambling of the case I peroxide (**5**) is in the same order with that of the decomposition.[12,28] Therefore, since the rate of the oxygen scrambling (k_{SC}) in the



Scheme 1.



Scheme 2.



Scheme 3.

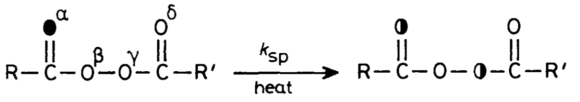
inversion product (**8**) [Scheme 5(*a*)] has been already known to be 2.85 × 10^{-5} s^{-1} in carbon tetrachloride at 45 °C,[30] the rate of the carboxy-inversion process of (**7**) is expected to be markedly greater than rates of the ^{18}O-scrambling in both peroxides (Scheme 4) and the inversion product [Scheme 5(*a*) and (*b*)]. Indeed, this has been found to be the case particularly in 2 mol dm^{-3} sulpholane–CCl_4, since a change of solvent from CCl_4 to 2 mol dm^{-3} sulpholane–CCl_4 does not vary the rate of the ^{18}O-scrambling (k_{sc}) in (**8**) but accelerates markedly the carboxy inversion of (**7**). This paper deals with the mechanism of the carboxy-inversion process based on the detailed analysis of our ^{18}O-tracer experiments using the peroxides (**7**)α, (**7**)δ and the related peroxides.

Results

Products of Thermal Decomposition of Diacyl Peroxides.—The decomposition of diacyl peroxides was carried out in solutions containing a peroxide of initial concentration 0.02 mol dm^{-3} in evacuated and sealed tubes placed in a thermostatted bath at a set temperature maintained to within 0.05 °C. Carbon tetrachloride was used as a non-polar solvent while sulpholane was the polar solvent, since sulpholane is polar (relative permittivity 44) and aprotic, yet has quite a low nucleophilicity and does not induce decomposition of both peroxides and the inversion products. However, since sulpholane is solid at room temperature (m.p. 27 °C), 2 mol dm^{-3} sulpholane–carbon tetrachloride solution was used for the thermolysis.

Thermal decomposition of (**7**) in carbon tetrachloride gave the inversion product (**8**) as a major product along with cyclohexyl benzoate, cyclohexene, carbon dioxide and benzoic acid as minor products (Scheme 6). Formation of a trace amount of cyclohexyl chloride was confirmed by CIDNP experiments; however, the yield was too small for accurate measurement. Thermal decomposition of (**7**) in 2 mol dm^{-3} sulpholane–carbon tetrachloride did not give any benzoic acid, but gave nearly the same amounts of the inversion products and the ester. In both solvents decomposition of (**7**) did not give phenyl cyclohexanecarbonyl carbonate, phenyl cyclohexanecarboxylate and cyclohexanecarboxylic acid. The distribution of the products at the decomposition of (**7**) and related peroxides are summarized in Table 1.

Kinetics of the Thermal Decomposition of Diacyl Peroxides.—First-order rate constants of the thermal decomposition of diacyl peroxides were determined by following the decrease of the peroxides by iodometry and are listed in Tables 2 and 3 together with activation parameters calculated from the linear Arrhenius plots. As expected, the rate of decomposition of (**7**) was found to be markedly higher than that of the ^{18}O-scrambling of the inversion product (**8**) formed, revealing that the peroxide (**7**) is quite suitable for the investigation of the carboxy-inversion mechanism by ^{18}O-tracer experiments.

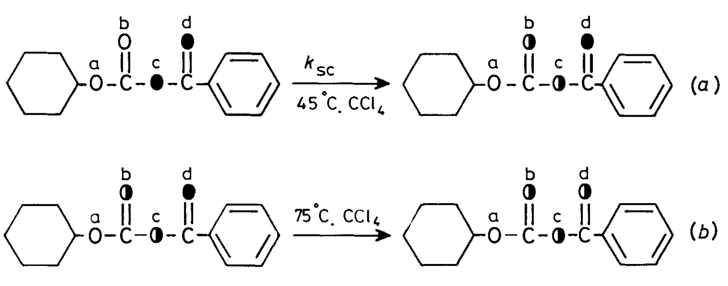


Case I peroxide R,R′ = Alkyl
Case II peroxide R = Alkyl; R′ = Aryl
Case III peroxide R,R′ = Aryl

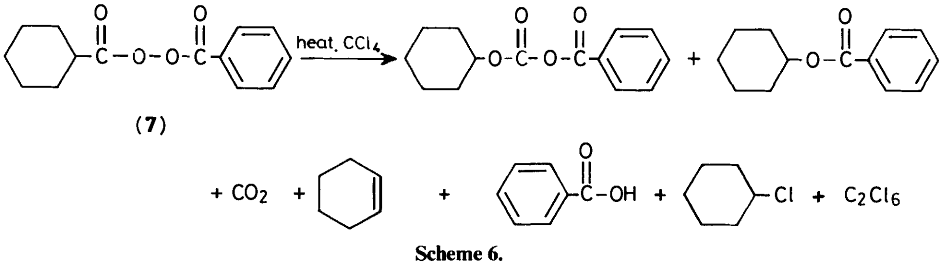
Scheme 4.

^{18}O-Tracer Experiments of Carboxy Inversion.—The peroxides (**7**)α and (**7**)δ labelled with ^{18}O at the α- and δ-oxygen atoms, respectively, were prepared from ^{18}O-labelled cyclohexanecarbonyl chloride and carbonyl-^{18}O-labelled perbenzoic acid prepared by treatment of carbonyl-^{18}O-labelled benzoyl peroxide with sodium methoxide by the method as we reported previously as shown in Scheme 7(*a*) and (*b*).[12] *m*-Chlorobenzoyl cyclohexanecarbonyl peroxides labelled with ^{18}O at the α- and δ-oxygens, (**11**)α and (**11**)δ, respectively, were also prepared by the same procedure. These peroxides labelled with ^{18}O-label were heated in evacuated and sealed tubes at 45 °C for *ca.* 6 half-lives of the peroxides. The inversion products were isolated and purified. Determination of ^{18}O-distribution in the inversion products was carried out according to a known method[12,22,30] which involves the reactions given in Scheme 8(*a*) and (*b*) to cleave the inversion products. The reaction products obtained in these reactions were subjected to our routine ^{18}O-analysis.[32] The results are listed in Table 5. The distribution of the ^{18}O-label of the carbonyl of the starting peroxide into the carboxy-inversion products can be calculated from the data in Table 5 and the percentage incorporations of the original ^{18}O-label into O-a, -b, -c, and -d of the carboxy-inversion products are summarized in Table 6.

Kinetics of ^{18}O-Scrambling in (**8**) *in Sulpholane*–CCl$_4$.—Since the rate of the ^{18}O-scrambling between O-b and -c of (**8**) in CCl$_4$ is already known, the rate in 2 mol dm^{-3} sulpholane–CCl$_4$ was measured. Specifically ^{18}O-labelled benzoyl cyclohexyl carbonate at O-c and -d atoms was prepared by the routine method as shown in Scheme 9 and heated in 2 mol dm^{-3} sulpholane–CCl$_4$ in evacuated and sealed tubes under the same conditions as for the decomposition of the corresponding diacyl peroxide (**7**). Under these conditions the carbonate (**8**) did not decompose. The carbonate recovered after being heated at 45 °C was treated with *N*-methylaniline to afford benzoic acid [Scheme 8(*b*)] which was purified and



Scheme 5.



Scheme 6.

Table 1. Products of the thermal decomposition of diacyl peroxides in solution.

					Yield (mol/mol%)			
					Inversion	Ester	Acid	Chloride
Peroxide	R	R′	Solvent	T/°C	$R{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'$	$R{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'$	$R'CO_2H$	RCl
(7)	c-C_6H_{11}	Ph	CCl_4	35.0	71.8	7.7	21.5	Trace
				40.0	71.7	7.8	21.7	Trace
				45.0	71.4			
				50.0	69.7	8.2	22.4	Trace
				55.0	69.5			
				60.0	68.6	8.7	23.3	Trace
				65.5	69.2	8.5	24.3	Trace
				70.0	68.4	8.4	24.5	Trace
			Sulpholane–CCl_4	30.0	53.9	46.2	0	0
				35.0	53.4	46.8	0	0
				40.0	53.4	48.0	0	0
				45.0	52.6	49.0	0	0
				55.0	52.1	48.9	0	0
				60.0	52.1	48.9	0	0
(11)	c-C_6H_{11}	C_6H_4Cl-m	CCl_4	45.0	74.0	6.5	20.0	a
(3)[b]	1-Apocamphyl	Ph	CCl_4	70.0	51	20	0	20[c]; 17[d]
(5)[e]	1-Apocamphyl	1-Apocamphyl	CCl_4	70.0	54.5	2.2	0	36[f]
			Sulpholane–CCl_4	70.0	66			
(9)[g]	c-C_6H_{11}	c-C_6H_{11}	CCl_4	50.0	h	47[h]	17	59
(13)[i]	Me_2CH	Ph	Cyclohexane	60.0	65	3	32	Trace
(15)[j]	Me_2CH	Me_2CH	CCl_4	50	27	20	13	79
(17)[k]	c-$C_3H_5CH_2$	$CH_2C_3H_5$-c	CCl_4	55	37	18	a	60

[a] Not determined. [b] Ref. 11. [c] 1-Apocamphyl chloride. [d] Chlorobenzene. [e] Ref. 22. [f] M. S. Kharasch, F. Engelman, and W. H. Urry, *J. Am. Chem. Soc.*, 1943, **65**, 2428. [g] Ref. 4. [h] All inversion product was decomposed to the ester. [i] Ref. 6. [j] Ref. 4. [k] Ref. 12.

Table 2. Kinetics of the thermal decomposition of benzoyl cyclohexanecarbonyl peroxide (**7**).

Solvent	T/°C	$k_d/10^{-5}\ s^{-1}$
CCl_4	35.0	2.14 ± 0.3
	40.0	3.62 ± 0.03
	44.0	6.00 ± 0.21
	44.0	6.28 ± 0.16
	45.0	6.72 ± 0.30
	45.0	7.28 ± 0.28
	50.0	13.6 ± 0.2
	55.0	23.2 ± 0.2
$\Delta H^{\ddagger}$/kcal mol^{-1}	45.0	24.0 ± 0.6
$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	45.0	-2.2 ± 1.8
Sulpholane–CCl_4	35.0	11.5 ± 0.1
	35.0	11.5 ± 0.4
	40.0	23.3 ± 0.2
	45.0	42.3 ± 0.2
$\Delta H^{\ddagger}$/kcal mol^{-1}	45.0	24.7 ± 1.0
$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	45.0	3.7 ± 3.2

Table 3. Kinetics of the thermal decomposition of 4-chlorobenzoyl cyclohexanecarbonyl peroxide (**11**).

Solvent	T/°C	$k_d/10^{-5}\ s^{-1}$
CCl_4	35.05	5.22 ± 0.03
	45.0	19.3 ± 0.3
	50.0	35.4 ± 1.2
$\Delta H^{\ddagger}$/kcal mol^{-1}	45.0	24.7 ± 0.2
$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	45.0	2.10 ± 0.63
Sulpholane–CCl_4	30.0	17.1 ± 0.5
	45.0	116 ± 0.9

Table 4. Differences in activation energy and entropy between the carboxy-inversion process and the processes forming the ester and the acid in the thermal decomposition of benzoyl cyclohexanecarbonyl peroxide (**7**).

Solvent	$\Delta\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
CCl_4 Carboxy-inversion – ester	-1.0 ± 0.2	0.33 ± 0.15
Carboxy-inversion – acid	-1.1 ± 0.1	-0.32 ± 0.04
Sulpholane–CCl_4 Carboxy-inversion – ester	-0.63 ± 0.06	-0.45 ± 0.05

subjected to ^{18}O-analysis. The results are summarized in Table 7.

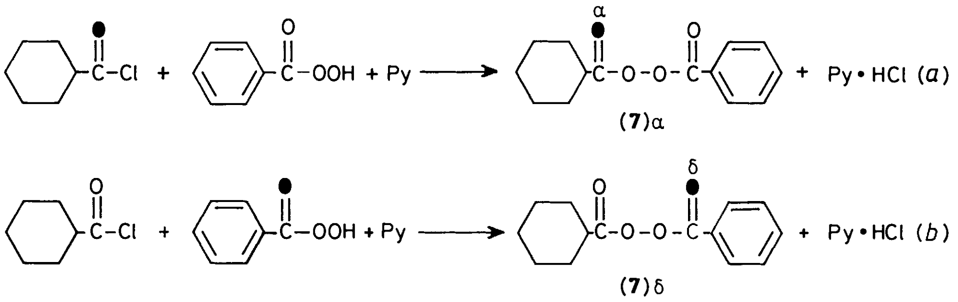
The ^{18}O-content of the benzanilide obtained from (**8**)cd ($t = 0$ in Table 7) upon treatment with aniline was found to be 1.476 excess atom% which was a bit smaller than that of the starting ^{18}O-labelled benzoic acid (1.484 excess atom%). This would take place during the purification step of the carbonate by recrystallization. The O-d of (**8**) after being heated for 381 min at 45 °C was found to have 1.457 excess atom% of ^{18}O. This small decrease of ^{18}O-content in O-d of (**8**) under these conditions indicates that slow ^{18}O-scrambling between O-c and -d [Scheme 5(*b*)] takes place concurrently with that between O-b and -c [Scheme 5(*a*)]. However, when one ignores such a small loss of ^{18}O in O-d, a good first-order rate constant of the ^{18}O-scrambling between O-b and -c [Scheme 5(*a*)], k_{sc}, may be obtained as shown in Table 7.

CIDNP Studies.—CIDNP n.m.r. spectra were recorded at 40–70 °C in evacuated and sealed n.m.r. tubes containing 0.02 mol dm^{-3} peroxide in CCl_4. The results are summarized in Table 8. A multiplet effect was observed in the thermolyses of symmetrical peroxides, (**9**) and (**15**), while only net polarization appeared in the thermolyses of unsymmetrical peroxides (**7**) and (**13**).

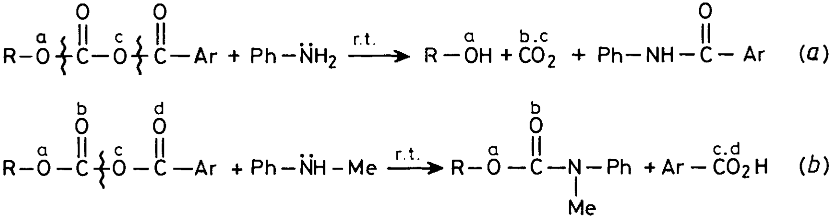
Table 5. ^{18}O-Tracer experimental results of the carboxy-inversion process of $R-\overset{\alpha O}{\overset{\|}{C}}-\overset{\beta}{O}-\overset{\gamma}{O}-\overset{O\delta}{\overset{\|}{C}}-R'$ in solution at 45 °C.

					^{18}O-Content (excess atom%)[b]					
Peroxide	R	R′	Solvent[a]	Reaction time/min	Original carbonyl-^{18}O label	$R\overset{a}{O}\overset{O}{\overset{\|}{C}}NHPh$	$CO_2^{b,c}$	$PhNH\overset{O^d}{\overset{\|}{C}}R'$	$R\overset{a}{O}\overset{O^b}{\overset{\|}{C}}NPh(Me)$	$R'CO_2^{c,d}H$
(7)α	c-C_6H_{11}	Ph	A	875	1.875	0.031	*c*	0.020	*c*	*c*
			B	175	1.875	0.038	11.872	0.000	0.822	0.128
			C	2 090	1.875	0.022	*c*	0.070	*c*	*c*
(7)β	c-C_6H_{11}	Ph	A	1 085	1.383	0.000	*c*	0.915	*c*	*c*
			B	194	1.383	0.000	0.460	0.957	0.035	0.677
			C	1 380	1.383	0.000	*c*	0.869	*c*	*c*
(11)α	c-C_6H_{11}	C_6H_4Cl-m	A	394	1.875	0.031	1.906	0.006	0.657	0.177
			A	363	1.569	0.020	*c*	*c*	0.656	*c*
			B	70	1.875	0.042	1.846	0.000	0.890	0.049
			B	60	1.569	0.025	*c*	0.000	0.755	0.044
(11)β	c-C_6H_{11}	C_6H_4Cl-m	A	392	1.254	0.000	*c*	0.833	0.027	0.584
			B	70	1.254	0.000	0.440	0.795	*c*	0.610
(9)	c-C_6H_{11}	c-C_6H_{11}	A	310	1.875	0.036	2.420	1.222	0.624	*c*
			B	110[d]	1.875	0.049	2.398	1.223	0.639	*c*
(5)	1-apocamphyl	1-apocamphyl	A	2 400[d]	2.43	0.56[f]	*c*	1.40	*c*	*c*
			A	4 800[d]	2.52	0.55[f]	*c*	1.44	*c*	*c*
			A	600[e]	2.40	0.50[f]	*c*	1.36	*c*	*c*
			B	960[d]	2.43	0.50[f]	*c*	1.44	*c*	*c*
			B	1 920	2.52	0.50[f]	0.73	1.47	*c*	*c*

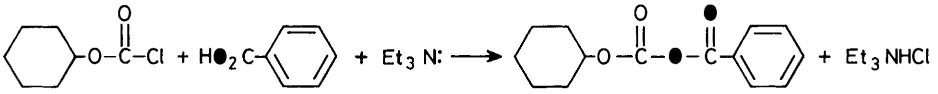
[a] A: CCl_4; B: 2 mol dm^{-3} sulpholane–CCl_4; C: Nujol. [b] ^{18}O-Content in CO_2 obtained from the pyrolysis of the compounds with $HgCl_2$ and $Hg(CN)_2$; error: ±0.005% except data in bottom five lines of which error is ±0.01%. [c] Not determined. [d] At 70 °C. [e] At 84.3 °C. [f] 1-Apocamphanol was subjected to analysis.



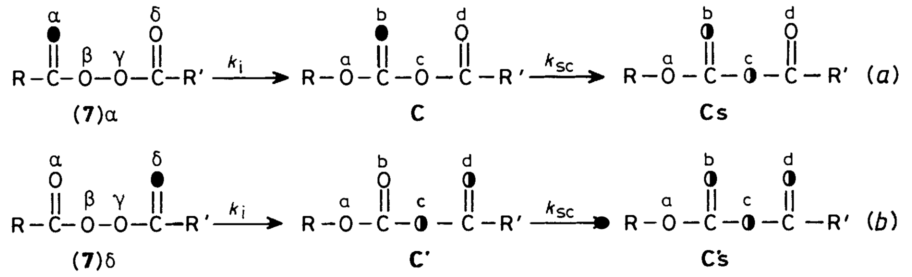
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

Table 6. Percentage incorporation of the original carbonyl ^{18}O-label of the starting peroxides into O-a, -b, -c, and -d of the carboxy-inversion products at 45 °C.

Entry	R′ in $c\text{-}C_6H_{11}\text{-}\overset{O^\alpha}{\overset{\|}{C}}\text{-}O\text{-}O\text{-}\overset{O^\delta}{\overset{\|}{C}}\text{-}R'$	Solvent[a]	Reaction time/min	% ^{18}O-incorporation into $R\text{-}O^a\overset{O^b}{\overset{\|}{C}}\text{-}O^c\overset{O^d}{\overset{\|}{C}}\text{-}R'$ a	b	c	d
1	Phenyl (**7**)α[b]	B	175	4	83	13	0
2	Phenyl (**7**)δ[b]	B	194	0	4	27	69
3	*m*-Chlorophenyl (**11**)α	A	394	3	78	19	0
4	*m*-Chlorophenyl (**11**)δ	A	392	0	5	29	66
5	*m*-Chlorophenyl (**11**)α	B	70	4	91	5	0
6	*m*-Chlorophenyl (**11**)δ	B	70	0	2	35	63
7	Cyclohexyl (**9**)[c]	A	310	3	66	66	65
8	Cyclohexyl (**9**)[c]	B	110	5	65	65	65

[a] A: CCl_4; B: 2 mol dm^{-3} sulpholane–CCl_4. [b] Greek-letter suffix denotes the position of the original ^{18}O-label in the starting peroxide. [c] Both carbonyl oxygen atoms of the starting peroxide ^{18}O-labelled.

Table 7. ^{18}O-Scrambling between O-b and -c of specifically c- and d-^{18}O-labelled benzoyl cyclohexyl carbonate (**8**)cd in 2 mol dm^{-3} sulpholane–CCl_4 at 45.0 °C.

Reaction time/s	^{18}O-Content in benzoic acid[a]	^{18}O-Content in benzanilide[b]
Starting material[c]	1.484	
0	1.474	1.476
1 800	1.461	
4 020	1.430	
8 700	1.381	
12 000	1.353	
15 300	1.327	
18 600	1.303	1.457
∞	1.113[d]	

$k_{sc} = 3.39 \pm 0.4 \times 10^{-5}\ s^{-1}$. [a] Obtained from the reaction in Scheme 8(*b*). [b] Obtained from the reaction in Scheme 8(*a*). [c] Benzoic acid which was used for the preparation of (**8**)cd by the reaction in Scheme 9.

Discussion

Verification of Denney's Carboxy-inversion Mechanism.—Under the reaction condition applied to the decomposition of the ^{18}O-labelled peroxides (**7**)α and (**7**)δ, one can safely assume that, (*a*) the oxygen scrambling (Scheme 4) in the peroxides during thermal decomposition of (**7**)α and (**7**)δ is quite negligible as described in the earlier context; (*b*) the scrambling of O-a of the inversion product (**8**) does not take place at all; (*c*) the oxygen scrambling between O-c and -d atoms of the inversion product (**8**) [Scheme 5(*b*)] takes place in a very minor extent but proceeds markedly slower than the decomposition of the peroxide (**7**); however, the ^{18}O-scrambling between O-b and -c of the inversion product (**8**) proceeds at the rate of *ca.* a quarter of that of decomposition of the peroxide (**7**) in CCl_4 and also at that of *ca.* one twelfth the rate of the decomposition in 2 mol dm^{-3} sulpholane–CCl_4. Such a large polar effect of the solvent on the ratio, k_{sc}/k_d, is associated with 5.8-fold increase in the rate of the decomposition of (**7**) (k_d) by changing solvent from CCl_4 to 2 mol dm^{-3} sulpholane–CCl_4, while the rate of the ^{18}O-scrambling [Scheme 5(*a*)] of (**8**)cd (k_{sc}) increases by a factor of only 1.2 for the same solvent change.

The ^{18}O-tracer experimental results shown in entries 1, 3, and 5 in Table 6 clearly reveal that the cyclohexyl group migrates preferentially to the α-oxygen of the peroxides. The small amount of ^{18}O-incorporation in O-a of the inversion product (**8**) resulting from (**7**)α undoubtedly takes place in the course of the carboxy-inversion process. Meanwhile, the ^{18}O-tracer experimental results shown in entires 2, 4, and 6 in Table 6 indicate clearly that only two thirds of the original ^{18}O-label of the δ-oxygen atom of the peroxides [(**7**)δ and (**11**)δ] is incorporated into O-d of the inversion products [(**8**) and (**12**)], respectively. The remaining one third of the original ^{18}O was not lost from O-d of the inversion products by equilibration between O-b and -c after the carboxy inversion in which the whole ^{18}O-label of δ-oxygen of the peroxide is specifically incorporated into O-d of the inversion product, but equilibrated with the other oxygen atoms during the carboxy-inversion processes. These complex ^{18}O-tracer experimental results seem to support Denney's carboxy-inversion mechanism,[20,22] if one takes the ^{18}O-scrambling between O-b and -c of the inversion products (**8**) and (**12**) into account. According to Denney's mechanism, the initial step of the thermolysis of peroxides, (**7**)α and (**7**)δ generates primarily the specifically ^{18}O-labelled inversion products, **C** and **C**′, respectively, which undergo ^{18}O-scrambling between O-b and -c eventually affording ^{18}O-scrambled alkyl acyl carbonates, **Cs** and **Cs**′, respectively. According to the mechanisms schemes shown in Scheme 10(*a*) and (*b*), the concentration of **C** may be expressed by equation (1), where P_0 denotes the initial concentration of the peroxide,

$$[C] = k_i/(k_{sc} - k_d)P_0[\exp(-k_d t) - \exp(-k_{sc} t)] \quad (1)$$

and k_i, k_{sc}, and k_d represent rate constants of the carboxy-

Table 8. CIDNP experiments in the thermal decomposition of benzoyl cyclohexanecarbonyl peroxide (**7**), bis(cyclohexanecarbonyl) peroxide (**9**), benzoyl isobutyryl peroxide (**13**), and bis(isobutyryl) peroxide (**15**).[a]

$R\text{–}O\text{–}\overset{\overset{O}{\|}}{C}\text{–}O\text{–}\overset{\overset{O}{\|}}{C}\text{–}R'$		Solvent				
$c\text{-}C_6H_{11}$	Ph	CCl_4	$\overline{(CH_2)_4\mathit{CH{=}CH}}$	$\overline{(CH_2)_5\mathit{C}}\mathit{H}Cl$	Ester Np	Inversion product Np
$c\text{-}C_6H_{11}$	$c\text{-}C_6H_{11}$	CCl_4	$\overline{(CH_2)_4\mathit{CH{=}CH}}$ AE	$\overline{(CH_2)_5\mathit{C}}\mathit{H}Cl$ AE	Ester Np	Inversion product Np
Me_2CH	Ph	CCl_4 or sulpholane–CCl_4	$\mathit{H_2C{=}CHCH_3}$ A E	$(CH_3)_2\mathit{CH}Cl$ A	Ester Np	Inversion product Np
Me_2CH	Me_2CH		$\mathit{H_2C{=}CH}CH_3$ EA EA	$(CH_2)_5\mathit{CH}Cl$ A	Ester Np	Inversion product Np

[a] The reaction was carried out in evacuated and sealed tubes. A, absorption; E, emission; Np, no polarization.

Table 9. Comparison of the yields of ^{18}O-retained inversion products, **C** and **C′**, calculated from the ^{18}O-tracer experimental results of the carboxy-inversion products of ^{18}O-labelled benzoyl cyclohexanecarbonyl peroxides (**7**)α and (**7**)δ shown in Schemes 9 and 10(*a*) with those calculated from k_d and k_i of (**7**) and k_{sc} of ^{18}O-labelled benzoyl cyclohexyl carbonate (**8**)cd in 2 mol dm^{-3} sulpholane–CCl_4 at 45.0 °C.

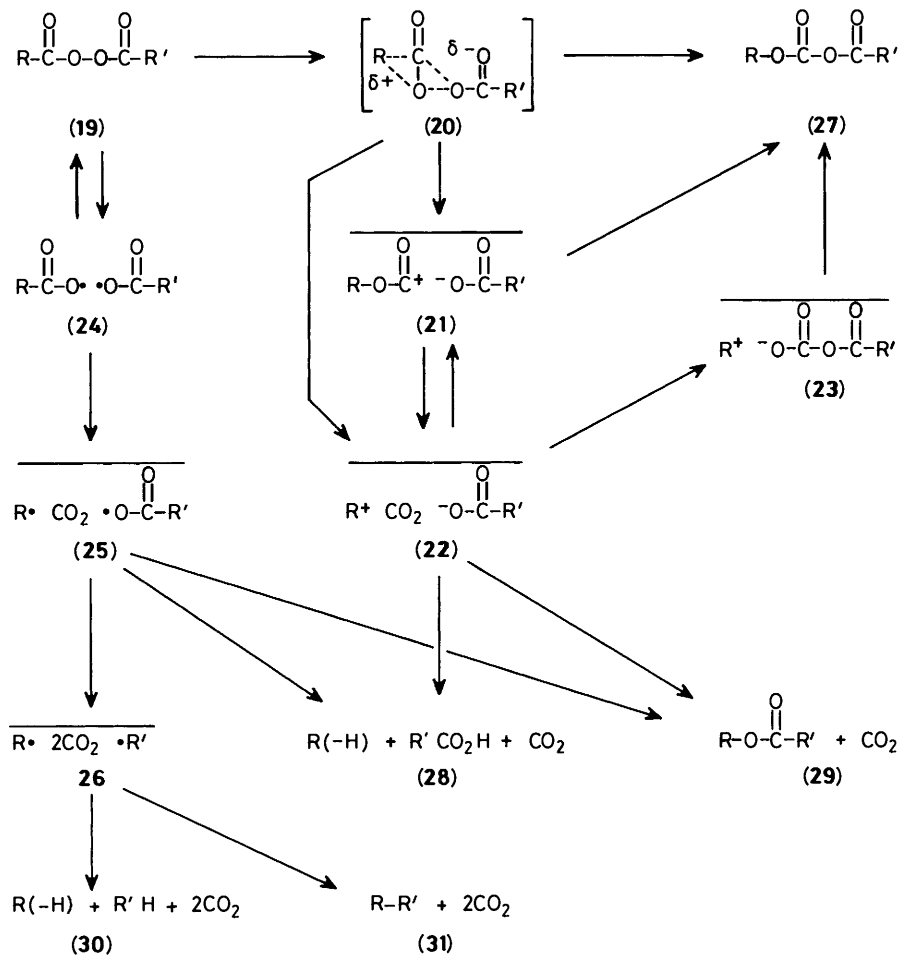
	[C]/([C] + [C$_s$]) from (7)α	[C′]/([C′] + [C$_s$′]) from (7)δ
^{18}O-Tracer results	0.73	0.74
Calc. from kinetic data	0.76	0.72

inversion, the ^{18}O-scrambling between O-b and -c of the inversion product and total decomposition of the peroxide, respectively. The value of k_i can be calculated from k_d and the yield of the carboxy-inversion product. The reaction time is represented by t. If the reaction schemes shown in Scheme 10(*a*) and (*b*) are responsible for the ^{18}O-experimental results of the carboxy-inversion of (**7**), [C]/([C] + [Cs]) and [C′]/([C′] + [Cs′]) calculated based on the tracer experimental results of entries 1 and 2 in Table 6 must be identical with those calculated from the kinetic results according to equation (1). Indeed, as shown in Table 9 the values obtained by these two different methods are in good agreement, revealing that the Denney's mechanism is quite acceptable. This is much more clearly demonstrated by the ^{18}O-tracer experiments using the peroxides (**11**)α and (**11**)δ as shown in entries 3–6 in Table 6, since the value of k_d/k_{sc} for (**11**) is much greater than that of (**7**) and hence the ^{18}O-tracer experimental results for (**11**) are much less masked by the complex ^{18}O-scrambling of the inversion product than those of (**7**), that is to say, although the rate of the ^{18}O-scrambling between O-b and -c of (**8**) is known not to change by the introduction of substituents into the phenyl ring,[30] the rate of the decomposition (k_d) of the corresponding diacyl peroxide (**7**) increases by a factor of 2.7 on introduction of Cl group on the *meta*-position of the phenyl ring, *i.e.* the peroxide (**11**).

The Nature of the Carboxy-inversion Process.—All the conceivable paths for the thermal decomposition of diacyl peroxides are shown in Scheme 11.[10–14,16,21] The thermal decomposition is believed to proceed through a single rate-determining step resulting in a polar intermediate which, in the subsequent step, is then partitioned into radical and ionic reaction paths.[10,11,13,14] As mentioned in the previous context, O-a in the carboxy-inversion product is not equilibrated with the other three oxygens under the conditions applied to the decomposition of the corresponding peroxides. The scrambling of O-d of the inversion product with O-b and -c is negligible in the thermal decomposition of the peroxide, the rate (k_d) of which is in the order of 10^{-5} s^{-1} at 45 °C. Thus, Table 10 summarizes the extent of incorporation of the original ^{18}O-label of α-oxygen of the starting peroxide into O-a of the inversion product and the incorporation of ^{18}O-label of δ-oxygen of the starting peroxide into O-d of the inversion product together with relative rates of decomposition, k_d^{rel}.

Incorporation of an ^{18}O-Label in O-d of the Carboxy-inversion Product Obtained from δ-Oxygen-^{18}O-Labelled Peroxide.—O-d of both the inversion products (**8**) and (**12**) is not scrambled under the condition applied to the decomposition of the peroxides, (**7**)δ and (**11**)δ, respectively. O-d of (**8**) retains only 66% of the original ^{18}O-label of (**7**)δ (Table 5). The possible intermediates leading to the ^{18}O-scrambled inversion product are the ion pairs (**21**) and (**22**) as shown in Scheme 11. This ^{18}O-experimental result reveals that 32% [100 − 2 × (100 − 66) = 32] of (**8**) is afforded directly *via* (**20**), while the remaining 68% of (**8**) is generated from the ion pairs (**21**) and (**22**). Therefore, the factors which stabilize these ion pairs seem to increase the yield of ^{18}O-scrambled carboxy-inversion product. However, the inversion product (**8**) obtained from (**7**)δ was found to contain ^{18}O at the O-d in the same content obtained from (**11**)δ which should give a longer-lived ion pair (**21**) which has a better chance to equilibrate the ^{18}O-label in the anionic counterpart than the ion pair (**21**) generated from (**7**)δ. Furthermore the pattern of the ^{18}O-tracer data is not affected by the change of solvent from CCl_4 to a polar solvent, 2 mol dm^{-3} sulpholane–CCl_4 in the carboxy-inversion process of both (**7**)δ (Table 5) and (**11**)δ (entries 4, 6 in Table 6). The somewhat lower ^{18}O-content in O-d of (**8**) obtained from (**7**)δ in Nujol than that obtained in CCl_4 may be due to the undesired ^{18}O-scrambling shown in Scheme 5(*b*) rather than an increase of the recombination of (**21**) to afford ^{18}O-scrambled inversion product in this viscous medium, because of the prolonged reaction time (Table 5). The unexpected lack of effects of the polarity and viscosity of the medium on the ^{18}O-incorporation of the original ^{18}O-label into O-d will be discussed in detail in connection with the stability of the intermediates (**21**) and (**22**) in the next section.

Since the decomposition of relatively stable peroxides (**3**) and (**5**), was carried out at a high temperature (Table 5) for a long



Scheme 11.

Table 10. Effects of structure of diacyl peroxides and the nature of the solvent on the thermal decomposition of ^{18}O-labelled diacyl peroxides at 45 °C.

Case[a]	Peroxide R	R′	Solv.[b]	k_{sp}/k_d	k_d^{rel} at 45 °C[c]	Polar-solvent effect on k_d[d]	Percentage ^{18}O-incorporation in O-a of carboxy-inversion product (%)[e]	Percentage ^{18}O-incorporation in O-d of carboxy-inversion product (%)[f]
I	(**5**) 1-Apocamphyl	1-Apocamphyl	A	0.67[g]	0.01	2.9[h]	20[h]	58[h]
			B	0.31[g]			20[h]	59[h]
I	(**9**) Cyclohexyl	Cyclohexyl	A	0.01[i]	2.9	3.3	3	65
			B		9.5		5	65
I	(**17**) Cyclopropyl-methyl	Cyclopropyl-methyl	A	0.00[j]	0.73[k]		20[j]	62[j]
II	(**3**) 1-Apocamphyl	Phenyl	A	0.05[l]	0.007[l]		3[h,l]	33[h,l]
II	(**7**) Cyclohexyl	Phenyl	A	0.00	1.000		3	66
			B	0.00	6.1	6.1	4	69
			C	0.00			4	63
II	(**11**) Cyclohexyl	*m*-Chlorophenyl	A	0.00	2.8	6.0	3	66
			B	0.00	16		4	63
III	(**1**) *p*-Methoxyphenyl	*m*-Nitrophenyl	D				0[m]	66[n]

[a] Classification of diacyl peroxide according to ref. 28. [b] A, CCl_4; B, 2 mol dm^{-3} sulpholane–CCl_4; C, Nujol; D, $SOCl_2$. [c] The rate of the decomposition of (**7**) in CCl_4 is taken as the standard. [d] Ratio of k_d in 2 mol dm^{-3} sulpholane–CCl_4 to that in CCl_4. [e] Percentage ^{18}O-incorporation in O-a of carboxy-inversion product from the α-^{18}O-label of the starting peroxide. [f] Percentage ^{18}O-incorporation in O-d of the carboxy-inversion product from δ-^{18}O-label of the starting peroxide. [g] Ref. 28. [h] At 70 °C. [i] Ref. 31. [j] Ref. 13. [k] Ref. 34. [l] Ref. 31. [m] Ref. 20. [n] Ref. 22.

time, O-d equilibrates with O-b and -c of the inversion products during the decomposition of peroxides after the carboxy-inversion. O-b, -c, and -d of the inversion products obtained by the thermal decomposition of (**9**) and (**17**)[13] contain the same amount of the original carbonyl ^{18}O-label of the starting peroxides (entries 7 and 8 in Table 6). This seems to result in the complete scrambling of ^{18}O-label among O-b, -c, and -d of the inversion products after decomposition of the peroxides [carbonyl-^{18}O-labelled (**9**) and (**17**)], though the control experiments have not yet been carried out.

Incorporation of ^{18}*O-label in O-a of the Carboxy-inversion Product Obtained from α-Oxygen-*^{18}*O-labelled Peroxide.*—O-a in all the inversion products listed in Table 10 does not equilibrate with the other three oxygen atoms under the conditions of the thermolysis of these peroxides. Therefore, the ^{18}O-incorporation in O-a of the inversion product reflects directly the event which takes place during the carboxy-inversion process.

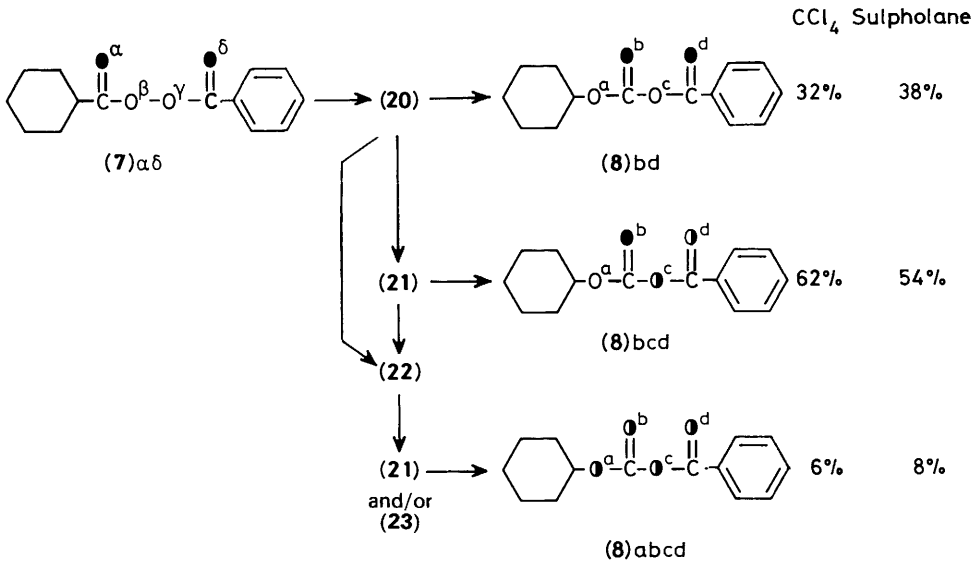
The following three routes are conceivable for the ^{18}O-incorporation into O-a of the inversion product resulted from the peroxide labelled with ^{18}O on the α-oxygen. (*a*) The ^{18}O-scrambling takes place in the peroxide (Scheme 4) prior to the carboxy-inversion process. (*b*) The radical pair (**25**) may give the ^{18}O-scrambled ion pair (**22**) *via* a single-electron transfer[33] which is eventually converted into ^{18}O-scrambled carboxy-inversion product (**27**) through (**21**) or (**23**). (*c*) The initial polar intermediate (**20**) may dissociate to the ion pair (**21**) in which ^{18}O-scrambling does not yet take place in the cationic counterpart. Further dissociation of the cationic part in (**21**) may give the intermediate (**22**) of which association *via* (**21**) or (**23**) affords (**27**) in which O-a contains the ^{18}O-label of the α-oxygen of the starting peroxide. Actually, the carboxy inversion of all the peroxides except (**1**)α labelled with ^{18}O at the α-oxygen listed in Table 10 gave the inversion products in which O-a retained the original ^{18}O to some extent (3–20%).

The extent of the contribution of the route (*a*) can be estimated based on the value of k_{sp}/k_d shown in Table 10. Since the value of k_{sp}/k_d decreases markedly in the order case I peroxide > case II peroxide > case III peroxide, the route (*a*) is important only for case I peroxides. The large value of k_{sp}/k_d for the peroxide (**5**) reveals that the route (*a*) is responsible for substantial amount of incorporation of the original ^{18}O into O-a of the inversion product of the carbonyl-^{18}O-labelled peroxide (**5**). The incorporation of only 3% of the original ^{18}O of α-^{18}O-labelled peroxide (**3**)α into O-a of (**4**) should be also due to the reaction shown in the route (*a*), since the value of k_{sp} is 5% of k_d. The route (*a*) is also partly responsible for a little ^{18}O-incorporation into O-a of the inversion product of the carbonyl ^{18}O-labelled peroxide (**9**). However, the route (*a*) may be ruled out for the other remaining peroxides listed in Table 10, since k_{sp}/k_d values for these peroxides are zero.

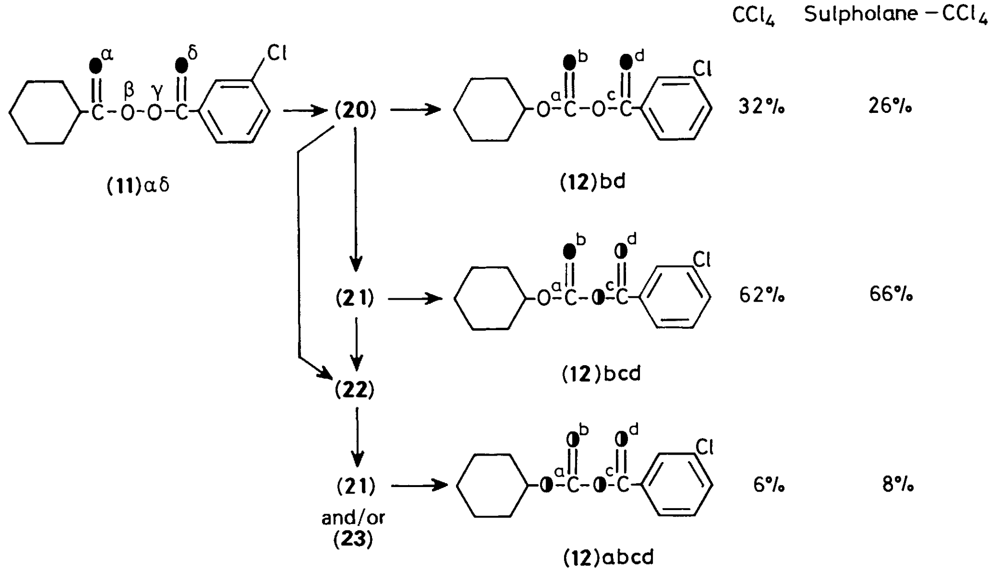
The reaction path involving single-electron transfer, (**19**) ⟶ (**24**) ⟶ (**25**) ⟶ (**22**) ⟶ (**28**) and (**29**) has been verified by the CIDNP by Lawler *et al.*,[34] in the thermolysis of *m*-chlorobenzoyl t-butylacetyl peroxide. Taylor *et al.*,[14] also detected ^{13}C CIDNP signals of the ester in which the alkyl portion underwent the Wagner–Meerwein rearrangement during the thermolysis of *m*-chlorobenzoyl cyclobutanecarbonyl peroxide to support the existence of this path. However, we could not detect any CIDNP signal of ester (**29**) and inversion product (**27**) on the ^{1}H n.m.r. spectra taken during the thermal decomposition of peroxides, (**3**), (**5**), (**7**), (**13**), and (**17**), thus ruling out the possibility shown in the route (*b*) for the decomposition of (**7**) and (**9**). The same amount of ^{18}O-incorporation into O-a of both carboxy-inversion products obtained from the α-^{18}O-labelled peroxides, (**7**)α and (**9**)α, is inconsistent with the route (*b*), since the intermediate (**25**) for the peroxide (**7**) is much longer lived and the single-electron transfer in it much easier to take place than that for the peroxide (**9**).

Thus, the small amount of ^{18}O-incorporation in O-a of (**8**) and (**12**) formed from peroxides, (**7**)α and (**11**)α, can be best explained by the route (*c*). For example, the incorporation of 3% of the ^{18}O-label of (**7**) into O-a of (**8**) in the thermolysis of (**7**)α in CCl_4 suggests that 6% of the total (**8**) is afforded from the ion pair (**22**). The amount of the carboxy-inversion product formed from (**22**) can be calculated from the data in Table 10 for the reaction of other peroxides. Here again, the change of solvent from CCl_4 to 2 mol dm^{-3} sulpholane–CCl_4 does not increase the ^{18}O-content of O-a of these inversion products as observed in the ^{18}O-content of O-d of the same inversion products from (**7**)α and (**11**)α. This increase of the polarity of the solvent, however, not only accelerates the rate of decomposition of the peroxide (**7**) by a factor of six (Table 10) but also changes substantially the product distribution, *i.e.* for the inversion product: 71 ⟶ 53%, for the ester: 8 ⟶ 49%, and for the acid and the alkene: 22 ⟶ 0% (Table 1). In the polar solvent, the lifetime of the ion pair (**21**) must be longer than in CCl_4 for it to have much chance of collapsing to the ion pair (**22**). Similarly, the ion pair (**21**) from (**11**) should be longer-lived than that from (**7**). However, O-a of both (**8**) and (**12**) from (**7**)α and (**11**)α contain nearly the same amount of ^{18}O. The increase in the viscosity of the medium should increase the yield of the cage products, whereas the ^{18}O-incorporation into O-a of (**8**) from (**7**)α is inert to the change of medium from CCl_4 to Nujol (Table 10). According to this mechanism of the route (*c*), one can estimate how three intermediates, (**20**), (**21**), and (**22**), contribute in the formation of the inversion products of different ^{18}O-distribution in the thermal decomposition of the hypothetical peroxide (**7**)αδ in CCl_4 at 45 °C if one superimposes the ^{18}O-tracer experimental results of both (**7**)α and (**7**)δ in Table 10 as shown in Scheme 12. The same calculation can be performed for the peroxide (**11**) based on the data in Table 10 (Scheme 13). The change of polarity and viscosity of solvent and substituent on the peroxide does not change practically the ratio of (**8**)bd, (**8**)bcd, and (**8**)abcd but changes substantially the total yield of (**8**). The stabilization of the ion pair (**21**) by the polar solvent raises the activation-energy barrier to afford the inversion product, while increasing the chance for the cyclohexyloxycarbonyl cation to decarboxylate, generating the ion pair (**22**). Indeed, the differences in the enthalpy of activation ($\Delta\Delta H^{\ddagger}$) between the formation of (**8**) and that of decarboxylated products, *i.e.* the ester, and the alkene and the acid, is found to be reduced from 1 to 0.6 kcal mol^{-1} by changing the solvent from CCl_4 to 2 mol dm^{-3} sulpholane–CCl_4 (Table 4). The oxygen atom of sulpholane may interact with cyclohexyl cation to assist decarboxylation of both (**20**) and (**21**). The co-ordination of sulpholane to cyclohexyl cation, however, increases the activation-energy barrier to recapture carbon dioxide, eventually to decrease the yield of (**8**)abcd and increase the yield of the ester. The absence of polar-substituent effects on the extent of the contributions of the three ion pairs in the formation of the carboxy-inversion product from (**7**)αδ, *i.e.* quite similar results of (**11**)αδ shown in Scheme 13 and of (**7**)αδ in Scheme 12, can be explained in the same way as the polar-solvent effect mentioned above. These observations indicate that decarboxylated products in the thermolyses of both (**7**) and (**11**) are formed by the ionic reaction path. On the other hand, in the thermolysis of (**5**) which gives very unstable strained carbocations in its ionic degradation path, the yield of the inversion product (**6**) increases on changing the solvent from CCl_4 to 2 mol dm^{-3} sulpholane–CCl_4 (Table 1), suggesting that the decarboxylated products of this reaction are of radical origin. The same solvent change causes a reduction of k_{sp}/k_d from 0.67 to 0.31, but exactly the same amount of oxygen-18 originating in the peroxide (**5**) is incorporated into O-a of (**6**) in both media despite the difference in polarity. This fact reveals that route (*c*) is partly responsible for the incorporation of the ^{18}O-label in O-a of (**6**) in the thermolysis of carbonyl-^{18}O-labelled (**5**) in 2 mol dm^{-3} sulpholane–CCl_4, while route (*a*) is still the major path. A much greater polar solvent effect on k_d of (**7**) than of (**5**) supports the above argument.

Earlier we reported that although the ^{18}O-scrambling (Scheme 4) does not take place during the thermal decomposition of cyclopropanecarbonyl peroxide (**17**) labelled with ^{18}O at the carbonyl ($k_{sp} \ll k_d$), (**17**) gave the inversion product, (**18**), in which the O-a retains 20% of the original ^{18}O-label.[13] Since this peroxide decomposes unusually readily unlike other



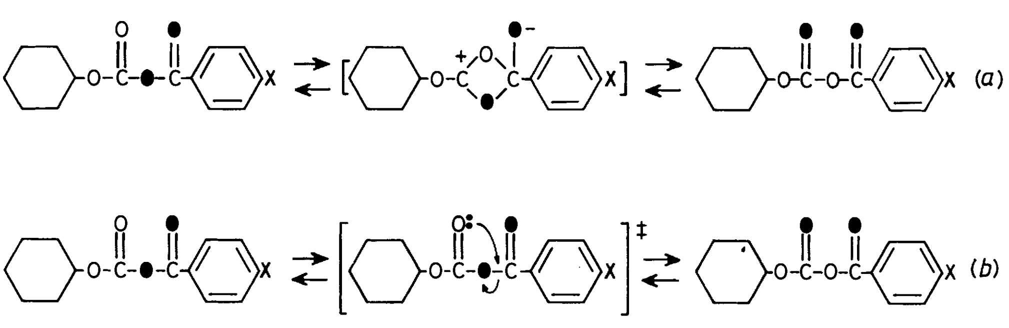
Scheme 12. Origins of the carboxy-inversion products with different ^{18}O-distributions in the thermal decomposition of the carbonyl-^{18}O-labelled peroxide, (7)αδ, in CCl_4 and 2 mol dm^{-3} sulpholane–CCl_4 at 45 °C (calculated based on the data in Table 9).



Scheme 13. Origins of the carboxy-inversion products with different ^{18}O-distributions in the thermal decomposition of the carbonyl-^{18}O-labelled peroxide, (11)αδ, in CCl_4 and 2 mol dm^{-3} sulpholane–CCl_4 at 45 °C (calculated based on the data in Table 9).

primary cycloalkylacetyl peroxides,[34] the decomposition of (17) would proceed nearly exclusively *via* a two-bond fission process *via* (20). Therefore, the incorporation of ^{18}O into O-a of (17) would proceed *via* route (3) *via* (22). Taylor *et al.*, have proved that the intervention of the ion pair (22) in a different manner, *i.e.* detection of the inversion product which has a rearranged alkyl group (*via* the Wagner–Meerwein rearrangement) in the thermal decomposition of *m*-chlorobenzoyl cyclobutanecarbonyl peroxide and the related peroxides. After we had finished this work, Leffler reported that when carbonyl-^{13}C-labelled *m*-chlorobenzoyl cyclobutanecarbonyl peroxide was decomposed in supercritical carbon dioxide, the ^{13}C of the carbonate carbonyl of cyclomethylcarbinyl *m*-chlorobenzoyl carbonate, *i.e.* the carboxy-inversion product formed *via* the ion pair (22), underwent *ca.* 12% exchange with solvent carbon dioxide.[21]

Formation of Decarboxylated Products.—Except acetyl peroxide,[35] case I peroxides have not hitherto been known to give CIDNP signals of ester. CIDNP signals of esters have been observed in thermal decomposition of case II peroxides bearing primary alkyl groups[35–37] or strained cycloalkyl groups[14] and case III peroxides.[38,39] However, nobody has yet successfully detected any CIDNP signals of the ester during thermal deomposition of any case II peroxide in which the R group is either a secondary or tertiary alkyl group. In this case, the ester is formed from the ion pair (22) rather than radical pair (26). Among case II peroxides which bear secondary alkyl groups, benzoyl isobutyryl peroxide (13) and benzoyl cyclohexanecarbonyl peroxide (7) behave quite differently in the CIDNP decomposition experiments in CCl_4 (Table 8). The peroxide (13) gave very strong net polarization on tne ^1H n.m.r. signals of propene and prop-2-yl chloride, while the peroxide (7) did not exhibit any CIDNP signal other than an extremely weak signal of net polarization of cyclohexyl chloride. These results suggest that propene is derived from the radical pair (25), however, prop-2-yl benzoate is formed from the ion pair (22) in the



Scheme 14.

thermolysis of the peroxide (**13**). Meanwhile both cyclohexene and cyclohexyl benzoate are formed from the ion pair (**22**) exclusively in the thermolysis of the peroxide (**7**). This may be explained by the difference in the ionization potential of two alkyl radicals prop-2-yl 7.90; cyclohexyl 7.66 eV). Thus, the partitioning of the polar intermediate (**20**) is very sensitive to the change in the ionization potential of the alkyl group.

There is a notable solvent effect on the reactivities of the ion pair (**22**) formed in the thermal decomposition of the peroxide (**7**). As shown in Tables 1 and 4, both the alkene (E1 product) and ester (S_N1 product) are formed from the ion pair (**22**) (R = cyclohexyl, R′ = phenyl) at almost the activation energy in CCl_4. However, only the ester is formed in good yield. Obviously the naked benzoate anion acts as a strong base in CCl_4 and abstracts a proton from cyclohexyl cation. In the presence of sulpholane, the oxygen co-ordinates with the carbocation to decrease the acidity of the α-proton and also substantially decreases the basicity of benzoate anion, thus retarding the rate of E1 reaction of the ion pair. The thermolysis of suitable diacyl peroxide provides a good system in which to examine the polar-solvent effect on the reactivity of ion pair in aprotic solvents.

Mechanism of ^{18}O*-Scrambling of Alkyl Acyl Carbonate.*—Previously, we suggested the following stepwise mechanism involving a zwitterionic intermediate for the intramolecular ^{18}O-scrambling between O-b and -c of alkyl acyl carbonate, *i.e.* a carboxy-inversion product, based on the rate of ^{18}O-scrambling (k_{sc}) for the three alkyl *p*-substituted benzoyl carbonate (**8**)x (X = Me, H, CN) being actually the same [Scheme 14(*a*)].[30] However, the rate constant for ^{18}O-scrambling, k_{sc}, has been found to increase by a factor of only 1.2 by the change of the solvent from CCl_4 to 2 mol dm^{-3} sulpholane–CCl_4. The lack of both polar-solvent and substituent effects on k_{sc} of (**8**)x may suggest the transition state of this ^{18}O-scrambling in (**8**) is not as polarized as the zwitterionic intermediate. Thus, we would like to propose concerted mechanism [Scheme 14(*b*)] for this ^{18}O-scrambling in an alkyl acyl carbonate which proceeds in CCl_4 even at room temperature.

Conclusions

(*a*) The detailed ^{18}O-tracer experimental results on the carboxy-inversion of (**7**) reveal that Denney's mechanism is basically correct.[20,22]

(*b*) Case II peroxides, (**7**) and (**11**), decompose almost exclusively *via* an ionic path even in CCl_4. The ^{18}O-tracer experiments revealed that at least three kinds of ion pair are involved in the carboxy-inversion process of these peroxides. The extent of the contributions of these ion pairs have been determined to be 32% for (**20**), 62% for (**21**), and 6% for (**22**) in the carboxy inversion of (**7**) in CCl_4 (Scheme 12). This ratio was found to be rather insensitive to both polar-solvent and substituent effects (Schemes 12 and 13).

(*c*) In the carboxy inversion of the case I peroxide (**5**), the ion pair (**22**) does not contribute in the reaction in CCl_4, but contributes in the reaction in 2 mol dm^{-3} sulpholane–CCl_4. Decarboxylated products of this peroxide are of radical origin.

(*d*) The ion pair (**22**) is responsible for 40% of the formation of the carboxy-inversion product in the thermolysis of the case I peroxide (**17**) in CCl_4.[13] Since (**17**) decomposes mainly *via* a radical path, the presence of the single-electron-transfer path in the radical pair (**25**) to afford the ion pair (**22**) is conceivable.

(*e*) The polar-solvent effect on the partitioning of the ion pair (**22**) generated from the peroxide (**7**) is remarkable.

(*f*) The concerted mechanism [Scheme (14(*b*)] is proposed for the ^{18}O-scrambling of benzoyl cyclohexyl carbonate.

Experimental

Infrared spectra were taken with Hitachi 260-5 infrared spectrophotometer. Mass spectra were recorded on Hitachi RMU-6MG mass spectrometer equipped with MG-141B gas inlet unit. N.m.r. spectra were recorded on JEOL H-100 n.m.r. spectrometer. Melting points were measured by use of a Yanaco MP instrument and are not corrected. All preparations and manipulation of peroxides and inversion products were carried out in a cold room at 4 or −20 °C.

Materials

α-Oxygen-^{18}O*-labelled Benzoyl Cyclohexanecarbonyl Peroxide* (**7**)α.—A mixture of cyclohexanecarbonyl chloride (31.5 g), ^{18}O-enriched water (3.9 g; *ca.* 4 atom%) and anhydrous dioxane (100 cm^3) was heated at 100 °C overnight. The mixture was evaporated under reduced pressure to leave an oil, which was treated with freshly distilled $SOCl_2$ (40 g) under reflux for 2 h. The resulting crude ^{18}O-labelled cyclohexanecarbonyl chloride was distilled under reduced pressure, b.p. 75–76 °C (19 mmHg) to give colourless oil (26.9 g) the ^{18}O-content of which was determined as benzanilide obtained by treating a small amount of the chloride with aniline.[32]

To a solution of ^{18}O-labelled cyclohexanecarbonyl chloride (8.15 g) in CH_2Cl_2 (10 cm^3) was added perbenzoic acid in $CHCl_3$ (0.38 mol dm^{-3}; 160 cm^3) at −20 °C. Pyridine (4.9 g) in CH_2Cl_2 (10 cm^3) was added dropwise to the mixture with stirring and cooling below −20 °C. The mixture was stirred for 2 h at −20 °C and poured onto ice. The organic layer was separated, washed consecutively with dilute aqueous HCl, 5% aqueous $NaHCO_3$, and distilled water, dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The residue was dissolved in a minimal amount of hexane at 10 °C and cooled with solid CO_2–acetone. Crystals were formed which were collected, washed with cold hexane and again dissolved in a minimal amount of ether at 10 °C. The same volume of methanol was added and the solution was cooled with solid CO_2–acetone to afford colourless crystals, which were collected, washed with cold methanol and dried in a desiccator under vacuum at 4 °C; (7)α: m.p. 55 °C (decomp.), $\nu_{C=O}$ 1 770 and 1 800 cm^{-1}.

δ-^{18}O-Labelled Benzoyl Cyclohexanecarbonyl Peroxide (**7**)δ.—Compound (**7**)δ was prepared from carbonyl-^{18}O-labelled perbenzoic acid, cyclohexanecarbonyl chloride, and pyridine as mentioned above. The ^{18}O-perbenzoic acid was prepared by treating carbonyl-^{18}O-labelled benzoyl peroxide with sodium methoxide.[12]

Carbonyl-^{18}O-labelled Bis(cyclohexanecarbonyl) Peroxide (**9**).—This was prepared by the procedure described for the preparation of 1-apocamphoryl peroxide.[29] The crude product was recrystallized from hexane and ether–methanol in the same manner as for (**7**). This peroxide melts at *ca.* 5 °C and explodes at room temperature; $\nu_{C=O}$ 1 774 and 1 800 cm^{-1}. The iodometric titration of the purified peroxide showed more than 99% purity.

α-^{18}O-Labelled m-*Chlorobenzoyl Cyclohexanecarbonyl Peroxide* (**11**)α *and δ-^{18}O-Labelled* m-*Chlorobenzoyl Cyclohexanecarbonyl Peroxide* (**11**)δ.—These were synthesized by the same procedure as described for the preparation of (**7**)α and (**7**)δ.

Bis(isobutyryl) Peroxide (**17**)[5] *and Benzoyl Isobutyryl Peroxide* (**13**).[7]—These were prepared by the method reported by Lamb *et al.*[7] O-b and c-^{18}O-labelled cyclohexyl benzoyl carbonate (**8**)cd was prepared as reported previously.[30]

Kinetics of the Thermal Decomposition of Diacyl Peroxides.—The peroxide solution (0.02 mol dm^{-3}; 5 cm^3) was pipetted into eight Pyrex tubes. The tubes were connected to a vacuum line, degassed by freeze–pump–thaw cycles, repeated three times, and sealed. The tubes were immersed in a thermostatted bath kept within ±0.05 °C of 33–35 °C. The first tube was retrieved after a few minutes and suddenly cooled with solid CO$_2$–acetone (t = 0). The remaining tubes were taken out at regular time intervals. The tube was opened and the solution was transferred to a 100 cm^3 conical flask without any loss of the remaining peroxide by means of freshly distilled propan-2-ol (40 cm^3). Acetic acid (1 cm^3) and saturated aqueous KI (1 cm^3) was added to the mixture, which was then heated for 15 min on a hotplate up to the incipient boiling point. The iodine thus liberated was titrated immediately with 0.02 mol dm^{-3} $Na_2S_2O_3$ solution. The excellent linear first-order kinetic plot was obtained for all cases over two half-lives of the peroxide.

Product Analysis of the Thermal Decomposition of Diacyl Peroxides.—A 0.02 mol dm^{-3} solution of the peroxide in CCl$_4$ or 2 mol dm^{-3} sulpholane–CCl$_4$ was heated for six half-lives of the peroxide in a thermostatted bath as mentioned above. Concentration of the inversion product ($\nu_{C=O}$ 1 750 and 1 805 cm^{-1}), the ester ($\nu_{C=O}$ 1 719 cm^{-1}) and the acid ($\nu_{C=O}$ 1 700 cm^{-1}) were determined by i.r. carbonyl stretch absorption. The yield of cyclohexene was determined by n.m.r. spectroscopy from the intensity of the alkene proton signal.

^{18}O-Tracer Investigation of Carboxy Inversion.—^{18}O-Labelled peroxide was allowed to decompose as described in the kinetic experiments for *ca.* six half-lives. The reaction mixture was washed with cold 2% aqueous NaHCO$_3$ and water, dried (Na$_2$SO$_4$), filtered and evaporated under reduced pressure at 0–4 °C. The oily residue was recrystallized by the addition of hexane. The crystals were collected, washed with cold hexane and dried in a desiccator under vacuum to give the pure crystalline carboxy-inversion product. In the reaction of the peroxide (**9**) the oily inversion product was treated with aniline or *N*-methylaniline without purification. The carboxy-inversion product was separated into two parts. A CCl$_4$ solution of half the amount of the inversion product and freshly distilled aniline were placed separately in different legs of a two-legged flask connected to a vacuum line. After being degassed by three freeze–pump–thaw cycles, the two solutions were mixed. The reaction in Scheme 8(*a*) took place immediately. The CO$_2$ evolved was transferred to a MS gas sampler by bulb-to-bulb distillation. The residue was filtered to give the crude crystalline anilide which was purified by recrystallization and subjected to MS analysis.[32] The filtrate was diluted with ether and passed through activated alumina. To the eluant was added phenyl isocyanate, and the mixture was refluxed overnight and evaporated. Cyclohexyl *N*-phenyl carbamate was isolated and purified by recrystallization from CH$_2$Cl$_2$–hexane and subjected to the routine ^{18}O-analysis.[32] The remaining half of the inversion product was treated with *N*-methylaniline in CCl$_4$ at room temperature. The mixture was extracted with 5% aqueous NaHCO$_3$. The organic layer was chromatographed through silica gel and washed with benzene to yield cyclohexyl *N*-methyl *N*-phenyl carbamate which was distilled under vacuum and subjected to ^{18}O-analysis. The NaHCO$_3$ extract was acidified and extracted with ether. The extract was washed with water, dried (Na$_2$SO$_4$), filtered, and evaporated to give the acid which was recrystallized from ether and hexane and subjected to ^{18}O-analysis.

Synthesis of ^{18}O-Labelled Benzoyl Cyclohexyl Carbonate, (**8**)cd, *and Kinetics of ^{18}O-Scrambling in* (**8**)cd.—These were carried out in 2 mol dm^{-3} sulpholane–CCl$_4$ in the same manner as reported previously.[30]

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