Thermal decomposition of diacyl peroxide. Part 10. Evidence for acyloxyl radical pair mechanism for ^{18}O-scrambling of ^{18}O-labelled cyclopropanecarbonyl peroxide

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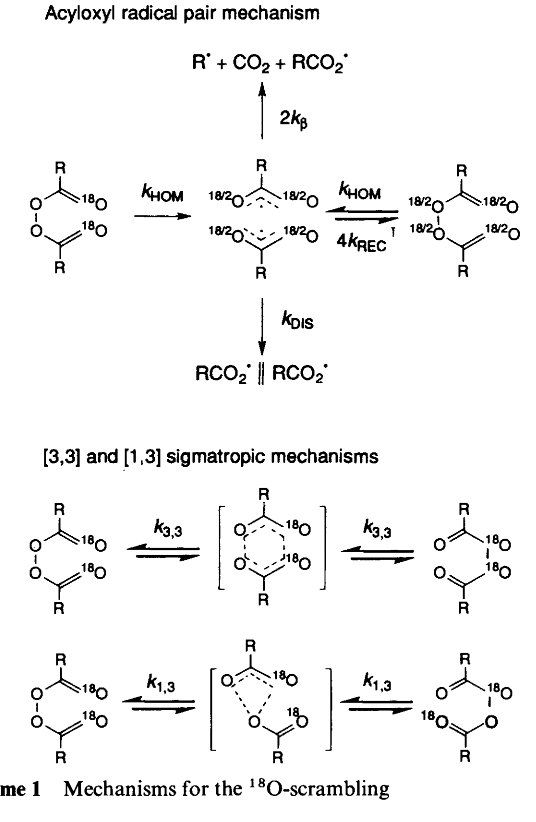
Oxygen-18 scrambling in carbonyl-^{18}O-labelled cyclopropanecarbonyl peroxide (CPO) and benzoyl cyclopropanecarbonyl peroxide has been suggested to take place *via* the recombination of intimate acyloxyl radical pair, based on the following experimental observations. (*i*) The rate of thermal decomposition of CPO decreased with the increase in the viscosity of hydrocarbon solvent; however, the rate of the ^{18}O-scrambling of CPO in Nujol, a highly viscous solvent, was found to be twice that in hexane. Examination of the effect of solvent viscosity on the rate of the decomposition of CPO by Pryor–Neuman's equation reveals that the ^{18}O-scrambling in CPO takes place almost solely through recombination of the intimate cyclopropanecarboxyl radical pair. In octane, the rate constant for dissociation of the intimate cyclopropanecarboxyl radical pair was estimated to be one order of magnitude greater than those for recombination and decarboxylation of the intimate acyloxyl radical pair. (*ii*) The enthalpy of activation for the decomposition of CPO was found to be 2.0–2.8 kcal mol^{-1} greater than that for the ^{18}O-scrambling of CPO in CCl_4 which corresponds to the energy barrier for dissociation of the intimate cyclopropanecarboxyl radical pair in the solvent cage. The entropy of activation for ^{18}O-scrambling was found to be small but positive in contrast to the large negative values of entropies of activation for usual concerted sigmatropic rearrangements. (*iii*) Successive substitution of the cyclopropyl groups of CPO with phenyl groups reduced markedly the rate of the ^{18}O-scrambling in the peroxides. This substituent effect is the same as that in the initial bond breaking type of the Cope rearrangement of homotropylidenes; however, opposite to that is the Cope rearrangements of open chain hexa-1,5-dienes in which a substantial extent of the new bond has been formed in the transition state.

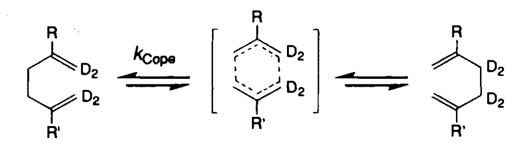
The mechanism of ^{18}O-scrambling in the ^{18}O-labelled diacyl peroxide (Scheme 1)[1–4] is quite an interesting problem, since it has created lively arguments in connection not only with the long standing problem of whether the homolytic decomposition of diacyl peroxide takes place *via* one bond O–O fission or the concerted multi-bond fission process,[5] but also with the mechanism of the Cope rearrangement of hexa-1,5-dienes (Scheme 2),[6–10] *i.e.* a kind of deuterium scrambling in hexa-1,5-dienes, since diacyl peroxides are 1,3,4,6-tetraoxahexa-1,5-dienes. The problem is also directly associated with both experimental[11–13] and theoretical[14] characterization of acyloxyl radicals.

Since Hammond and Soffer revealed concrete evidence for the homolytic O–O one bond fission for the thermal decomposition of benzoyl peroxide (BPO),[15] many attempts have been made to examine the mode of bond fission in the thermal decomposition of various diacyl peroxides, especially acetyl peroxide (APO).[16] Attempts to trap acetoxyl radicals with various radical scavengers were hardly successful,[16] though kinetic studies[17] and solvent viscosity effects[18] have suggested that APO is a one bond scission initiator. Meanwhile, Martin *et al.* reported that they had succeeded in trapping acetoxyl radicals with cyclohexene in the decomposition of APO.[19] Further, they succeeded in detecting ^{18}O-scrambling of APO during the thermal decomposition of carbonyl ^{18}O-labelled APO.[1] Assuming the acyloxyl radical pair mechanism (Scheme 1) in which the complete ^{18}O-equilibration in acetoxyl radicals has been postulated, they calculate the cage recombination of the acetoxyl radical pair in isooctane to be 38% at 80 °C.[1]


Acyloxyl radical pair mechanism

[3,3] and [1,3] sigmatropic mechanisms

Scheme 1 Mechanisms for the ^{18}O-scrambling



Scheme 2 The Cope rearrangement

The rate of ^{18}O-scrambling in both APO [1c] and BPO [1d] during the decomposition has been shown to increase with the increase in viscosity of the medium used, in keeping with the substantial solvent viscosity effect on the rate of decomposition of APO [18] supporting the acyloxyl radical pair mechanism.

On the other hand, Goldstein and co-workers have proposed the [3,3]- and [1,3]-sigmatropic mechanisms for the ^{18}O-scrambling of APO.[2] This idea originated from their presumed multi-bond breaking mechanism of APO.[20] Assuming that both the recombination and the dissociation of the acyloxyl radical pair in a solvent cage can be treated as first-order, Goldstein and co-workers have solved the first-order kinetics for the reactions shown in Scheme 1 which give two experimentally distinguishable ^{18}O-scrambling rate constants, *i.e.* total scrambling (k_{ts}) and random scrambling (k_{rs}), which correlate with the rate constants of the elemental processes involved in Scheme 1 by eqns. (1) and (2).[2] The fraction of

$$k_{ts} = k_{HOM}f_r + 2(k_{3,3} + k_{1,3}) \qquad (1)$$

$$k_{rs} = k_{HOM}f_r + 4k_{1,3} \qquad (2)$$

acyloxyl radical pair return (f_r) and the first-order rate constant for decomposition (k_d) are expressed in eqns. (3) and (4).

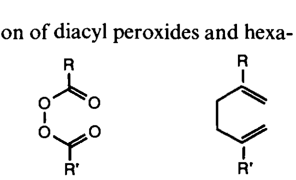
$$f_r = 4k_{REC}/(4k_{REC} + k_{DIS} + 2k_\beta) = 1 - k_d/k_{HOM} \qquad (3)$$

$$k_d = k_{HOM}(k_{DIS} + 2k_\beta)/(4k_{REC} + k_{DIS} + 2k_\beta) \qquad (4)$$

They then determined the two rate constants both in solution [2a] and in the gas phase.[2b] The occurrence of ^{18}O-scrambling of APO in the gas phase in which there is no cage effect is regarded as strong support for the sigmatropic mechanisms.

Meanwhile, we have suggested the acyloxyl radical pair mechanism for the ^{18}O-scrambling of 1-apocamphoryl peroxide and 1-apocamphoryl benzoyl peroxide based on the observations that the successive displacement of 1-apocamphoryl groups of 1-apocamphoryl peroxide by phenyl groups has retarded significantly the ^{18}O-scrambling, but not the decomposition.[3b] Based on these observations and other pertinent data on the thermal decomposition, we classified diacyl peroxides ($R\text{–}CO_2O_2\text{–}R'$) into Case I (R, R′: alkyl), Case II (R: alkyl: R′; aryl) and Case III (R, R′: aryl) and the general relationship between the stabilities of acyloxyl radicals, f_r and k_s have been postulated as shown in Table 1.[3b] From eqn. (3), the value of f_r depends on the relative values of k_{REC}, k_β and k_{DIS}. An energy barrier may be present in the recombination of the acyloxyl radical pair. Since aromatic acyloxyl radicals are more stable than aliphatic ones, recombination of an aromatic acyloxyl radical pair requires a greater activation energy than the aliphatic acyloxyl radical pair. Therefore, larger f_r values are expected for Case I peroxides than for Case II or III peroxides, although decarboxylation of the aliphatic acyloxyl radical is fast. On the other hand, since k_{DIS} is greater than both k_{REC} and k_β in the aromatic acyloxyl radical pair formed from a Case III peroxide, f_r and k_s become small despite the much longer lifetime of the aromatic acyloxyl radical pair [11–13,15] which would have a better chance of recombining in a solvent cage than the aliphatic acyloxyl radical pair. However, the mechanisms for the thermolysis of both 1-apocamphoryl peroxide and 1-apocamphoryl benzoyl peroxide are complex since the thermolysis proceeds *via* both polar and homolytic decomposition paths with comparable rates.[3b]

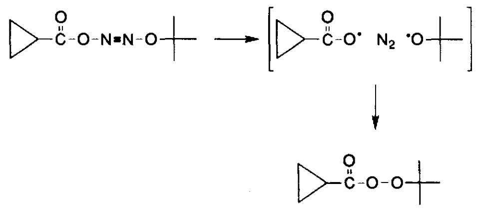
Table 1 Classification of diacyl peroxides and hexa-1,5-dienes



Case	*R*	*R′*	f_r [a]	k_s [b]	k_{Cope} [c]
I	Alkyl	Alkyl	Large	Large	Small
II	Alkyl	Aryl	Medium	Medium	Medium
III	Aryl	Aryl	Small	Small	Large

[a] Fraction of cage return of acyloxyl radical pair ($RCO_2{}^\bullet{}^\bullet O_2CR'$). [b] Rate constant for ^{18}O-scrambling of diacyl peroxides. [c] Rate constant for the Cope rearrangement of hexa-1,5-dienes.

Koenig *et al.* reported that cyclopropanecarboxyl–*tert*-butoxyl radical pairs, which were generated in hexane as shown in Scheme 3, combined to form *tert*-butyl cyclopropanecarbonyl peroxide in 21% yield in hexane while acetoxyl–*tert*-butoxyl radical pairs gave only 2.7% of the peroxyacetate, revealing that the cyclopropanecarboxyl radical is stable enough to combine with the *tert*-butoxyl radical in the solvent cage.[21] In order to further substantiate the above argument, we have chosen cyclopropanecarbonyl peroxide (CPO) to investigate the mechanism of ^{18}O-scrambling during the thermal decomposition of diacyl peroxide. Product analysis of the thermolysis of CPO has already been reported by Greig and Thynne.[22]



Scheme 3

The mode of ^{18}O-scrambling of diacyl peroxide has been diagnosed according to the following three criteria. (*i*) If the sigmatropic mechanism is responsible for the ^{18}O-scrambling, the rate of ^{18}O-scrambling would vary very little by a change in solvent viscosity. Alternatively, if the ^{18}O-scrambling occurs *via* the acyloxyl radical pair, both the rate of the ^{18}O-scrambling and decomposition of the peroxide would depend on the viscosity of the solvent in the opposite direction.[1,3,18] (*ii*) If the ^{18}O-scrambling proceeds *via* sigmatropic shifts,[7] the activation enthalpy for the ^{18}O-scrambling should be less than that for homolytic cleavage of the O–O bond because of the concertedness of the sigmatropic shifts.[9] (*iii*) Comparison of the structural effect on the rate of the ^{18}O-scrambling and that of the Cope rearrangement, a typical [3,3]sigmatropy,[7] should shed light on the mechanistic feature of the ^{18}O-scrambling.

Results

Kinetics of thermal decomposition of diacyl peroxides

Kinetics of the thermal decomposition of CPO and benzoyl cyclopropanecarbonyl peroxide (BCPO) have been determined by following the disappearance of the carbonyl stretching vibration absorption at 1780 and 1770 cm^{-1}, respectively, in both alkanes and CCl_4 (0.01–0.02 mol dm^{-3} peroxide). Linear first-order kinetic plots have been obtained up to 80% completion, revealing no induced decomposition through the chain reaction. Rate constants calculated by the least squares method (correlation coefficient >0.999) for CPO are listed in Tables 2 and 3 together with activation parameters. The rate constant for the decomposition of BCPO in CCl_4 has been determined to be $(5.65 \pm 0.10) \times 10^{-5}$ s^{-1} at 80 °C.

Table 2 Rate constants and activation parameters for thermal decomopsition and ^{18}O-scrambling of CPO in CCl_4

Temp./°C	$k_d/10^{-5}$ s^{-1}	$k_{ts}/10^{-5}$ s^{-1}	$k_{rs}/10^{-5}$ s^{-1}
65.0	0.608 ± 0.023	0.217 ± 0.004	0.289 ± 0.006
70.0	1.19 ± 0.005	0.420 ± 0.009	0.547 ± 0.015
75.0	2.44 ± 0.04	0.817 ± 0.080	1.02 ± 0.12
80.0	4.62 ± 0.03	1.46 ± 0.09	1.88 ± 0.13
$\Delta H^‡$/kcal mol^{-1} [a]	31.5 ± 0.4	29.5 ± 0.5	28.7 ± 0.1
$\Delta S^‡$/cal mol^{-1} K^{-1}	10.9 ± 1.1	2.7 ± 1.4	1.3 ± 0.3

[a] 1 cal = 4.184 J.

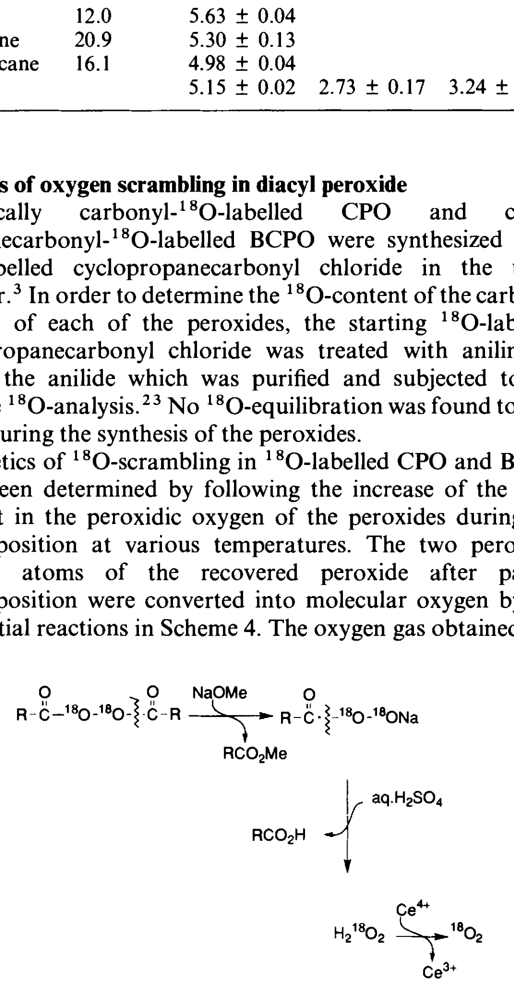
Table 3 Solvent viscosity effect on rate constants for thermal decomposition and ^{18}O-scrambling of CPO at 80 °C

Solvent	$(\eta/A_v)^{0.7}$	$k_d/10^{-5}$ s^{-1}	$k_{ts}/10^{-5}$ s^{-1}	$k_{rs}/10^{-5}$ s^{-1}
Hexane	5.00	6.50 ± 0.07		
Octane	7.82	6.02 ± 0.05	1.31 ± 0.12	1.65 ± 0.12
Decane	12.0	5.63 ± 0.04		
Dodecane	20.9	5.30 ± 0.13		
Tetradecane	16.1	4.98 ± 0.04		
Nujol		5.15 ± 0.02	2.73 ± 0.17	3.24 ± 0.31

Kinetics of oxygen scrambling in diacyl peroxide

Specifically carbonyl-^{18}O-labelled CPO and cyclopropanecarbonyl-^{18}O-labelled BCPO were synthesized from ^{18}O-labelled cyclopropanecarbonyl chloride in the usual manner.[3] In order to determine the ^{18}O-content of the carbonyl oxygen of each of the peroxides, the starting ^{18}O-labelled cyclopropanecarbonyl chloride was treated with aniline to afford the anilide which was purified and subjected to the routine ^{18}O-analysis.[23] No ^{18}O-equilibration was found to take place during the synthesis of the peroxides.

Kinetics of ^{18}O-scrambling in ^{18}O-labelled CPO and BCPO have been determined by following the increase of the ^{18}O-content in the peroxidic oxygen of the peroxides during the decomposition at various temperatures. The two peroxidic oxygen atoms of the recovered peroxide after partial decomposition were converted into molecular oxygen by the sequential reactions in Scheme 4. The oxygen gas obtained was introduced into the mass spectrometer to record peaks of m/z 32, 34 and 36. The two ^{18}O-scrambling rate constants, k_{ts} and k_{rs}, were computed from the mass spectral data by a non-linear least squares method according to eqns. (5)–(8).[2] Thus,



Scheme 4

$$R_1 = N_1/(1 - N_1 - N_2) \quad (5)$$

$$R_2 = N_2/N_1 \quad (6)$$

$$N_1 + 2N_2 = (c + p) - (c - p)\exp(-k_{ts}t) \quad (7)$$

$$N_2 = [(c + p)^2/4] - [(c^2 - p^2)/2]\exp(-k_{ts}t) + [(c - p)^2/4]\exp(-k_{rs}t) \quad (8)$$

excellent sets of k_{ts} and k_{rs} have been obtained in the thermal decomposition of CPO with the initial ^{18}O-content of 35.400 atom% in both hexane and Nujol at 80 °C (Table 2) and also in CCl_4 at various temperatures (Table 3). Since the ^{18}O-content (2.409%) was not high enough to determine k_{rs}, only k_{ts} was determined for benzoyl-^{18}O-labelled BCPO as (5.15 ± 0.08) × 10^{-6} s^{-1} in CCl_4 at 80 °C where R_1 is the ratio of mass spectral peak intensities of m/z 34:m/z 32, R_2 is the ratio of mass spectral peak intensities of m/z 36:m/z 34, N_1 is the mol fraction of $^{34}O_2$, N_2 is the mol fraction of $^{36}O_2$, c is the initial atom fraction of ^{18}O in the carbonyl oxygen of the peroxide, p is the initial atom fraction of ^{18}O in the peroxidic oxygen of the peroxide and t is time.

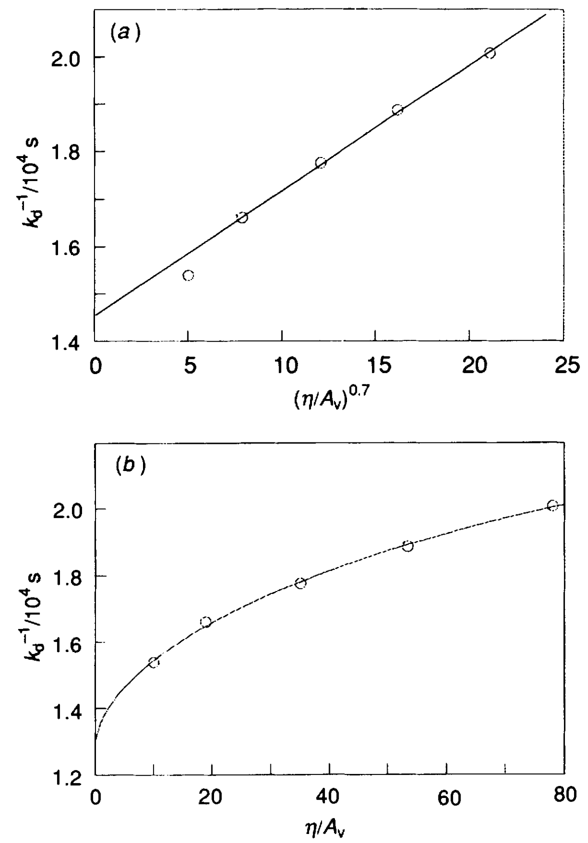


Fig. 1 Effects of solvent viscosity on rates of decomposition of CPO. (*a*) Pryor plot. (*b*) Pryor–Neuman plot. Solid lines are of theoretical curves.

Discussion

Solvent viscosity effect

The significant effects of solvent viscosity not only on k_{ts} and k_{rs} which increase, but also on k_d which decreases with the increase in solvent viscosity, suggest that both the decomposition and the ^{18}O-scrambling occurs *via* recombination of cyclopropanecarboxyl radical pair. Assuming that the rate constant for fragmentation of the geminate radical pair (k_β) is negligibly small, Pryor and Smith correlated the rates of the decomposition of several radical initiators with the viscosity of hydrocarbon solvents of the reaction by eqn. (9) where A_D is the

$$k_d^{-1} = k_{HOM}^{-1} + (4k_{REC}/k_{HOM}A_D)(\eta/A_v)^{0.7} \quad (9)$$

pre-exponential factor in the Arrhenius equation for diffusion of the acyloxyl radical pair, A_v is the pre-exponential factor in the Arrhenius equation for diffusive flow of solvent and η is the viscosity of the solvent.

When reciprocals of k_d values in Table 3 are plotted against $(\eta/A_v)^{0.7}$ values, only the point for hexane has been found not to satisfy eqn. (9) [Fig. 1(*a*)]. This suggests that the rate of decarboxylation of the cyclopropanecarboxyl radical (k_β) is significant compared with k_{DIS} and k_{REC} as pointed out by Neuman and Lockey who modified Pryor's equation to that expressed by eqn. (10) that contains k_β.[24] Upon treatment of

$$k_d{}^{-1} = k_{HOM}{}^{-1} + (4k_{REC}/k_{HOM}A_D)(\eta/A_v)^{0.64} \times [1 + (k_\beta/A_D)(\eta/A_v)^{0.64}]^{-1} \quad (10)$$

the experimental data listed in Table 3 with the Pryor–Neuman's equation [eqn. (10)] by means of a non-linear least-squares method, the following kinetic parameters have been obtained; *i.e.* $k_{HOM} = (7.69 \pm 0.27) \times 10^{-5}$ s^{-1}, $k_\beta/A_D = 0.0271 \pm 0.0138$ and $4k_{REC}/A_D = 0.0487 \pm 0.0118$. As shown in Fig. 1(*b*), the theoretical curve that provides a satisfactory fit for the experimental data involving the point of hexane was calculated with eqn. (10) and the above mentioned kinetic parameters.

According to the acyloxyl radical pair mechanism (Scheme 1), a fraction of cyclopropanecarboxyl radical pair regenerating CPO (f_r) can be calculated from experimentally observed values of k_d and k_{HOM} and eqn. (3) independent of the ^{18}O-scrambling experiments. The rate constants for the concerted ^{18}O-scrambling process of [1,3]- and [3,3] sigmatropies ($k_{1,3}$ and $k_{3,3}$) are then obtained by subtracting the value of $k_{HOM}f_r$ from k_{ts} and k_{rs} [eqns. (1) and (2)]. The results are listed in Table 4. Obviously, $k_{3,3}$ and $k_{1,3}$ are practically zero for the decomposition in octane, while the whole ^{18}O-scrambling shown in Table 3 can be explained solely by $k_{HOM}f_r$, *i.e.* the cage return of the cyclopropanecarboxyl radical pair in which four oxygen atoms are equivalent. If one assumes that k_{HOM} in *n*-alkanes (C_6–C_{14}) is identical to that in Nujol, the f_r value of the cyclopropanecarboxyl radical pair in Nujol can be calculated and then $k_{1,3}$ and $k_{3,3}$ can also be calculated in the same manner as in octane as mentioned above (Table 4). The rate constant for [3,3]sigmatropy ($k_{3,3}$) in Nujol is also zero.

Johnston *et al.* have reported that CPO is a multi-bond scission initiator in $CH_2ClCFCl_2$ based on their EPR experiments that the rate of the formation of PhCH(OOC-*cyclo*-C_3H_5)–N(*tert*-C_4H_9)–O$^\bullet$ during the thermolysis of CPO in the presence of *N*-benzylidene-*N*-*tert*-butylamine *N*-oxide at 52 °C was independent of the concentration of the *N*-oxide,[25] contrary to the thermolysis of BPO in the presence of the *N*-oxide in which the rate of the formation of PhCH(OOCPh)–N(*tert*-C_4H_9)–O$^\bullet$ increases with the concentration of the *N*-oxide.[26] The ratio of the rate constants, $k_{REC}:k_{DIS}:k_\beta$ for the thermolysis of CPO in octane at 80 °C has been calculated to be 1 : 11.5 : 1.5 from $k_{REC}/k_{HOM}A_D$ and k_β/A_D values obtained from the Pryor–Neuman's plot in Fig. 1(*b*) and f_r in Table 4. Thus, the rate of β-scission of cyclopropanecarboxyl radical (k_β) is found to be $0.13k_{DIS}$. Since k_{DIS} in usual solvents can be estimated to be in the order of 10^{10} s^{-1},[27] k_β for the cyclopropanecarboxyl radical is in the order of 10^9 s^{-1} at 80 °C. The value is comparable to that for the acetoxyl radical at 20 °C (1.3×10^9 s^{-1}).[13] If the rate of the reaction of the *N*-oxide with cyclopropanecarboxyl radical is the same as that for the 4-methoxybenzoyl radical (3.2×10^8 dm^3 mol^{-1} s^{-1} at 24 °C),[12b] the pseudo-first-order rate constant for the trapping reaction of cyclopropanecarboxyl radical with the *N*-oxide of 0.12 mol dm^{-3} concentration is estimated to be 3.8×10^7 s^{-1} at 24 °C. Since the activation energy for decarboxylation of the cyclopropanecarboxyl radical is undoubtedly less than that of benzoyloxyl radical, which has been reported to be 7.3–8.6 kcal mol^{-1},[12c] the minimum value of k_β for the cyclopropanecarboxyl radical at 24 °C is in the order of 10^8 s^{-1}. Thus, the decarboxylation of the cyclopropanecarboxyl radical is too fast to be trapped by the *N*-oxide at a concentration of 0.12 mol dm^{-3}.† Therefore, both the solvent viscosity effect on k_d of the peroxide and the ^{18}O-tracer experiment are more sensitive tests than the spin-trapping experiment using *N*-benzylidene-*N*-*tert*-butylamine *N*-oxide for the detection of the acyloxy radical pair formed in the initial stage of the thermal decomposition of some diacyl peroxide in which k_β is quite large.

Table 4 Calculated values of f_r, $k_{HOM}f_r$, $k_{3.3}$ and $k_{1,3}$ for thermolysis of CPO in octane and Nujol based on experimentally observed values of k_{ts}, k_{rs} and viscosity effects on k_d

Solvent	f_r[a]	$k_{HOM}f_r/10^{-5}$ s^{-1}	$k_{3,3}/10^{-5}$ s^{-1} [b]	$k_{1,3}/10^{-5}$ s^{-1} [b]
Octane	0.216	1.66	−0.17	0.00
Nujol	0.329	2.53	−0.08	0.18

[a] Calculated from the value of $k_{HOM} = 7.68 \times 10^{-5}$ s^{-1} and k_d values by eqn. (3). [b] Calculated by subtracting the value of $k_{HOM}f_r$ from the values of k_{ts} and k_{rs} according to eqns. (1) and (2).

Activation parameters

Generally, when an intramolecular rearrangement proceeds by a concerted mechanism, the enthalpy of activation for the rearrangement reaction ($\Delta H^\ddagger_{rearrangement}$) should be less than that ($\Delta H^\ddagger_{homolysis}$) for the homolytic scission–recombination process *via* a radical pair because of the energy gain due to the concertedness.[9] The value of $\Delta\Delta H^\ddagger$ defined by eqn. (11) may

$$\Delta\Delta H^\ddagger = \Delta H^\ddagger_{homolysis} - \Delta H^\ddagger_{rearrangement} \quad (11)$$

be significant in elucidating the mechanism of the ^{18}O-scrambling in CPO, a kind of intramolecular rearrangement. Namely, one can expect a substantial $\Delta\Delta H^\ddagger$ value for the sigmatropic mechanisms, while $\Delta\Delta H^\ddagger \approx 0$ for the acyloxyl radical pair mechanism. The enthalpy of activation for decomposition of CPO ($\Delta_d H^\ddagger$) is nearly identical to that for the homolysis of the O–O bond to form the cyclopropanecarboxyl radical pair ($\Delta H^\ddagger_{homolysis}$). Then, $\Delta\Delta H^\ddagger$ for the intramolecular rearrangement of the acyloxyl group, *i.e.* the ^{18}O-scrambling of CPO can be estimated by eqn. (12) and is compared with $\Delta\Delta H^\ddagger$ for the

$$\Delta\Delta H^\ddagger \approx \Delta_d H^\ddagger - \Delta_s H^\ddagger \quad (12)$$

Cope rearrangements of hexa-1,5-diene which is considered to be a typical [3,3]sigmatropy[7] as shown in Table 5.

The value of $\Delta\Delta H^\ddagger$ for the Cope rearrangements[6–10] are substantial, while the value of $\Delta\Delta H^\ddagger$ for the ^{18}O-scrambling of diacyl peroxides are extremely small. The apparent values of $\Delta\Delta H^\ddagger$ for the total (2.0 ± 0.6 kcal mol^{-1}) and the random (2.8 ± 0.4 kcal mol^{-1}) scrambling of CPO are identical within experimental error, suggesting that both the total and the random ^{18}O-scramblings occur at the same rate-determining step. Since *ca.* 2–3 kcal mol^{-1} is usually regarded as an activation enthalpy for the dissociation of a geminate pair from a cage of the usual solvent,[16,28] a $\Delta\Delta H^\ddagger$ value of 2–2.8 kcal mol^{-1} in the ^{18}O-scrambling of CPO can be regarded as the enthalpy of activation which is required for the dissociation of the cyclopropanecarboxyl radical pair out of the solvent cage. Apparently, $\Delta\Delta H^\ddagger$ values for both the total scrambling (0.7 kcal mol^{-1}) and the random scrambling (0.8 kcal mol^{-1}) of APO in the gas phase are almost zero within experimental error (Table 5).[2b]

The activation entropy for the Cope rearrangements is negative in accordance with the large value of $\Delta\Delta H^\ddagger$. On the other hand, the activation entropies of the ^{18}O-scrambling in the peroxides are very small positive values, supporting the acyloxyl radical pair mechanism, *i.e.* the freedom would increase only a little in the transition state with the acyloxyl

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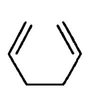
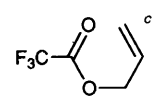
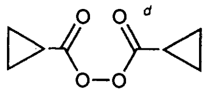
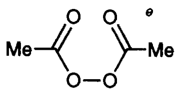
† The major path forming PhCH(OCO-*cyclo*-C_3H_5)-N-($C_4H_9{}^t$)-O$^\bullet$ would be the polar addition reaction of cyclopropaneformic acid to the *N*-oxide followed by hydrogen abstraction of the hydroxylamine. Johnston *et al.* also explained in terms of the initial ionic addition of cyclopropanecarboxylate to the *N*-oxide.[25]

Table 5 Comparison of $\Delta\Delta H^{\ddagger}_{\text{homolysis-rearrangement}}$[a] and entropy[b] of activation for some intramolecular rearrangements

Cope rearrangements		^{18}O-Scramblings	
	[c]	[d] in CCl_4	[e] in Gas Phase
Chair transition state[f] $\Delta\Delta H^\ddagger = 28.7$ $\Delta S^\ddagger = -13.8$ Boat transition state[g] $\Delta\Delta H^\ddagger = 17.5$ $\Delta H^\ddagger = -3.0$	Dioxa-Cope rearr. $\Delta\Delta H^\ddagger =$ *ca.* 23.5 $\Delta S^\ddagger = -9.8$	Total scrambling $\Delta\Delta H^\ddagger = 2.0 \pm 0.6$ $\Delta S^\ddagger = 2.7 \pm 1.4$ Random scrambling $\Delta\Delta H^\ddagger = 2.8 \pm 0.4$ $\Delta S^\ddagger = 1.3 \pm 0.3$	Total scrambling $\Delta\Delta H^\ddagger = 1.3 \pm 1.1$ $\Delta S^\ddagger = 4.3$ Random scrambling $\Delta\Delta H^\ddagger = 1.5 \pm 1.6$ $\Delta S^\ddagger = 3.5$

[a] Defined by eqn. (14); kcal mol^{-1}. [b] Cal mol^{-1} K^{-1}. [c] Ref. 9. [d] Ref. 6*d*. [e] E. S. Lewis and E. R. Newman, *J. Am. Chem. Soc.*, 1968, **90**, 662. [f] This work. [g] Ref. 2*b*.

radical pair mechanism. Thus a very small $\Delta\Delta H^\ddagger$and small positive value of $\Delta S^\ddagger$ for the ^{18}O-scrambling are best explained by the acyloxyl radical pair mechanism rather than the sigmatropic mechanisms in keeping with the solvent viscosity experimental results mentioned above.

Substituent effect

If the [3,3]sigmatropic shift plays a major role in the ^{18}O-scrambling in diacyl peroxides as proposed by Goldstein and co-workers,[2] the substituent effect on the ^{18}O-scrambling in diacyl peroxides is expected to follow a similar trend to that of the Cope rearrangement of hexa-1,5-dienes, carbon analogues of diacylperoxides. Hexa-1,5-dienes are also classified into three cases depending on the substituents at 2- and 5-positions, in the same manner as defined in the classification of the diacyl peroxides (Table 1). Relative rates for the Cope rearrangement ($k_{\text{Cope}}^{\text{rel}}$) are hexa-1,5-diene (Case I):2-phenylhexa-1,5-diene (Case II):2,5-diphenylhexa-1,5-diene (Case III) = 1:69:4900 at 189.9 °C.[10] This accelerating effect of the phenyl group is rationalized in terms of the phenyl groups increasing the extent to which a new bond between the 1- and 6-positions of the diene is formed, while decreasing the extent of breaking the old bond between the 3- and 4-positions at the transition state of the reaction to resemble the cyclohexane-1,4-diyl structure.[9,10]

On the contrary, successive substitution of the cyclopropyl groups in CPO by phenyl groups reduces the rate of ^{18}O-scrambling, *i.e.* relative k_{ts} values of CPO (Case I) : BCPO (Case II) : BPO[1d] (Case III) = 11 : 4 : 1. This trend is, however, in good agreement with the substituent effect in the initial bond breaking type of the Cope rearrangements of homotropilidenes and barbaralanes.[6c] This substituent effect on the ^{18}O-scrambling of diacyl peroxide, opposite to that of the usual Cope rearrangement of acyclic hexa-1,5-diene derivatives (Fig. 2) again cannot be explained by the sigmatropic mechanisms (Schemes 2 and 3), but is consistent with the acyloxyl radical pair mechanism as mentioned below.

The quantitative treatment of the substituent effect on the ^{18}O-scrambling serves as evidence to support our earlier hypothesis of the acyloxyl radical pair mechanism for the ^{18}O-scrambling, which is based on the postulation that the recombination of the acyloxyl radical pair requires some small activation energy. The amount of Gibbs' energy of activation required to recombine a pair of acyloxyl radicals in the solvent cage should depend on the stability of the acyloxyl radical pair. In fact, the combination of 4-methoxybenzoyloxyl radicals has been proposed to have an activation energy of 10.4 kcal mol^{-1} in CH_3CN, in which the radicals are significantly more stable than in CCl_4.[11b] Since the Case I peroxide produces very unstable acyloxyl radicals, the Gibbs' energy of activation for the recombination is less than those for Case II and Case III peroxides, and therefore f_r is larger than those of the other cases. In Case III peroxides, since the recombination of the acyloxyl radical pairs, which are stabilized by the aryl group, requires a larger activation energy than those of the Case I peroxides, both k_{REC} and k_β are small in comparison with k_{DIS} and therefore the dissociation process of the acyloxyl radical pair predominates over the recombination and results in the slow ^{18}O-scrambling.

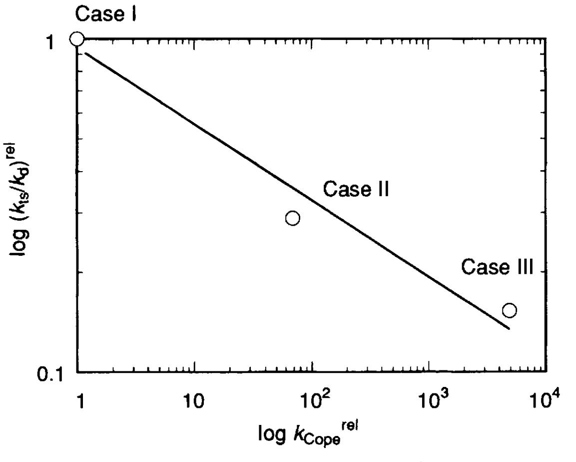


Fig. 2 Logarithmic plots of $(k_{\text{ts}}/k_{\text{d}})^{\text{rel}}$ *versus* $k_{\text{Cope}}^{\text{rel}}$

The relative rates of the ^{18}O-scrambling for CPO, BCPO and BPO agree well with the postulate supporting the acyloxyl radical pair mechanism, in which the rate of ^{18}O-scrambling is determined by both k_{HOM} and f_r. The relative rates of the ^{18}O-scrambling of the present peroxides are not controlled by the substituent effect on k_{HOM} but on f_r. This is verified by the fact that the $k_{\text{ts}}/k_{\text{d}}$ value decreases in the order of CPO (Case I) > BCPO (Case II) > BPO (Case III).‡ If the ^{18}O-scrambling for these peroxides takes place by the acyloxyl radical pair mechanism, eqn. (13) is obtained. Since $k_{\text{DIS}} > k_\beta$ for these

$$k_{\text{ts}}/k_{\text{d}} = 4k_{\text{REC}}/(k_{\text{DIS}} + 2k_\beta) \qquad (13)$$

peroxides, one obtains eqn. (14). The fact that the value k_{ts} of

$$k_{\text{ts}}/k_{\text{d}} \approx 4k_{\text{REC}}/k_{\text{DIS}} \qquad (14)$$

CPO is identical to that of *exo*-7-norcaranecarbonyl peroxide (NCPO) may suggest that the size of the acyloxyl radical does not have much influence on the magnitude of k_{DIS}.[29] Therefore, the free energy of activation for the diffusion of these acyloxyl

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‡ Since Ingold *et al.* revealed that the benzoyloxyl radical is quite reactive toward hydrocarbons,[12] the small k_{ts} value for BPO in isooctane reported by Hargis and Martin[1d] may be partly due to the reaction of benzoyloxyl radical with the solvent.

radicals ($cyclo$-$C_3H_5CO_2^{\cdot}$ and $PhCO_2^{\cdot}$) can be deemed to be approximately the same. Thus, the logarithm of the relative values of k_{ts}/k_d is expressed by eqn. (15) (80 °C), where the

$$\log[(k_{ts}/k_d)/(k_{ts}/k_d)_{BPO}] \approx \log[k_{REC}/k_{REC}(BPO)] = -[\Delta_{REC}G^{\ddagger} - \Delta_{REC}G^{\ddagger}(BPO)]/2.303RT = -(6.21 \times 10^{-4})\Delta\Delta_{REC}G^{\ddagger} \quad (15)$$

reference peroxide is BPO (Case III peroxide) where $\Delta_{REC}G^{\ddagger}$ and $\Delta_{DIS}G^{\ddagger}$ represent the Gibbs' energies of activation of the recombination and the dissociation of the acyloxyl radical pair, respectively. That is, log $(k_{ts}/k_d)^{rel}$ is in direct proportion to the difference between the Gibbs' energies of activation for the recombination of the acyloxyl radical pairs generated from Case I, II and III peroxides. Thus, one can calculate from eqn. (15) that $\Delta_{REC}G^{\ddagger}$ for BPO is 0.87 and 1.32 kcal mol^{-1} greater than those for BCPO and CPO, respectively.

Fig. 2 shows a plot of log $(k_{ts}/k_d)^{rel}$ *versus* the logarithm of relative rates of the Cope rearrangements of hexa-1,5-dienes (log $k_{Cope}{}^{rel}$). The linear relationship between $\Delta\Delta_{REC}G^{\ddagger}$ and $\Delta\Delta_{Cope}G^{\ddagger}$ may be rationalized in terms of the following. (*i*) The driving force of the Cope rearrangement of the open chain hexa-1,5-dienes is the new bond formation between C-1 and C-5 in which the transition state is stabilized by phenyl groups at the 2- and 5-positions, *i.e.* the new bond formation assists the breaking of the old bond. (*ii*) The driving force of the ^{18}O-scrambling is the bond-breaking of the very unstable peroxidic linkage to release the electronic strain of the peroxide bond generating the acyloxyl radical pair and the ^{18}O-scrambling is controlled by the size of $\Delta_{REC}G^{\ddagger}$. In the Cope rearrangement of a highly strained bicyclic ring system, the breaking of the old bond to release the Baeyer strain seems to be the driving force of the rearrangement.[6c] This argument has been further verified by the ^{18}O-tracer experiments using phthaloyl peroxide which is a Case III diacyl peroxide that produces an unescapable acyloxyl radical pair upon heating.[30]

Conclusion

Our experimental results on the solvent viscosity effect, activation parameters and the substituent effect on the rates of thermal decomposition and the ^{18}O-scrambling support the acyloxyl radical pair mechanism for the ^{18}O-scrambling of CPO, BCPO and BPO.

Experimental

General

IR spectra were recorded on an Hitachi 260–50 IR photospectrometer. Mass spectra for ^{18}O-analysis were taken from an Hitachi RMU-6MG mass spectrometer. NMR spectra were recorded on an Hitachi R-20 NMR spectrometer. Carbon tetrachloride (Kanto Chemicals, JIS-GR grade) was purified in the usual manner.[31] Hydrocarbon solvents were purchased from Tokyo Kasei Kogyo (TCI-SG, TCI-GR grade) and used without further purification. Thermolysis of diacyl peroxides has been carried out in Pyrex tubes, which were washed with dilute HF solution, subsequently by distilled water, dried in an oven and cooled just before use.

Cyclopropanecarbonyl peroxide (CPO)

Cyclopropanecarbonyl chloride (2 g) in 30 cm^3 of moist diethyl ether was placed in a 100 cm^3 three-necked flask equipped with a magnetic stirrer and then 0.9 g of sodium peroxide was added to the mixture with stirring and cooling in an ice bath. Water (10 cm^3) was added dropwise. After 2 h, the organic layer was separated and washed with water, dilute $NaHCO_3$ solution and water. The ether solution was cooled to −30 °C. Ice precipitated was removed by decantation. The ether solution was condensed to near dryness under vacuum below room temperature. The residue was dissolved in 10 cm^3 hexane and then cooled in a dry ice–acetone bath. Colourless crystals of CPO formed were collected and recrystallized several times from hexane and then with methanol in the same manner, mp 80–81 °C, $\nu(CCl_4)/cm^{-1}$ 1022, 1070, 1379, 1775, 1800 and 3105.

Benzoyl cyclopropanecarbonyl peroxide (BCPO)

A solution of 5.4 g of perbenzoic acid in 100 cm^3 of diethyl ether was placed in a 300 cm^3 three-necked flask equipped with a dropping funnel and a magnetic stirrer. Cyclopropanecarbonyl chloride (4.01 g) was added to the solution. Pyridine (3.09 g) in 100 cm^3 of diethyl ether was added slowly with stirring and cooling in a dry ice–acetone bath. After 2 h, the reaction mixture was poured into ice water. The organic layer was separated and washed with a dilute $NaHCO_3$ solution and water at 4 °C. The ether layer was dried and evaporated. The oily residue was dissolved in a minimum volume of hexane and cooled with a dry ice–acetone bath to crystallize the peroxide. The supernatant was removed by decantation and the crystalline residue was recrystallized from hexane followed by methanol several times in the same manner, mp −5 °C; $\nu(CCl_4)/cm^{-1}$ 1770 and 1800; δ_H 0.9–1.3 (4 H, m, CH_2 in cyclopropyl), 1.5–2.0 (1 H, m, methine in cyclopropyl) and 7.8–8.2 (5 H, m, phenyl).

Kinetics of thermal decomposition of peroxides by iodometry

5 cm^3 of 0.02 mol dm^{-3} peroxide solution was pipetted into each of eight Pyrex tubes. The tubes were connected to a vacuum line, degassed by repeated freeze–pumping–thaw cycles and sealed. The tubes were immersed in a thermostatted bath within 0.05 °C. The first tube was picked up after 5 min and cooled by a dry ice–acetone bath ($t = 0$). Tubes were successively picked up at appropriate time intervals. Then each tube was opened and the mixture was transferred into a 100 cm^3 conical flask without any loss of the remaining peroxide by aid of 40 cm^3 of freshly distilled absolute propan-2-ol. 1 cm^3 of acetic acid and 1 cm^3 of saturated aq. KI solution were added to the mixture and heated at the boiling point for 15 min on a hot plate. Then the liberated iodine was titrated with 0.02 mol dm^{-3} $Na_2S_2O_3$ solution.

Kinetics of thermal decomposition of peroxides by IR

1 cm^3 of peroxide solution (0.02 mol dm^{-3}) was placed in each of 10 Pyrex tubes, degassed and sealed in the same manner as mentioned above. After the reaction, each of the tubes was opened and the solution was introduced into the IR liquid cell of 0.5 mm thickness. IR spectra in the carbonyl region (1860–1750 cm^{-1}) were recorded.

Kinetics of ^{18}O-scrambling in peroxides

The carbonyl-^{18}O-labelled peroxide was decomposed in the same manner applied for the kinetics of the decomposition. Each tube was charged with an appropriate amount of 0.025 mol dm^{-3} solution of the peroxide to leave *ca.* 50 μmols of undecomposed peroxide after heating for various time lengths. After the reaction, each of the tubes was opened and the mixture was transferred to a 50 cm^3 two-necked flask which was connected to a vacuum line and evaporated at room temperature under reduced pressure. To the residue was added (over 15 min) 15 cm^3 of 0.0133 mol dm^{-3} sodium methoxide solution in methanol under cooling in an ice–water bath and stirred for 5 min under an argon stream. Then 7.5 cm^3 of 8 mol dm^{-3} aq. solution of H_2SO_4 was added (*ca.* 30 min) with stirring under cooling in an ice–water bath. The reaction mixture was stirred for 1 day at room temperature. The reaction flask was connected to a vacuum line. The other neck was equipped with an L-shape tube containing $Ce(SO_4)_2$ powder. The air in the flask was carefully removed by freeze–pumping–thaw cycles (less than 10^{-4} Torr). Then the stop cock of the reactor was closed and ceric sulfate powder was added to the solution by

Table 6 Kinetic runs of ^{18}O-scrambling of CPO

65.0 °C in CCl_4 (c = 0.354; p = 0.002)								
Reaction time/s	0	28 800	57 600	90 000	122 400	158 400	194 760	244 800
R_1	0	0.024	0.043	0.063	0.083	0.105	0.125	0.147
R_2	0.004 0.010	0.058	0.066	0.069	0.071	0.073	0.074	0.079
70.0 °C in CCl_4 (c = 0.354; p = 0.002)								
Reaction time/s	0	14 000	28 000	43 640	57 600	75 600	93 720	118 800
R_1	0.005	0.019	0.040	0.058	0.072	0.1000	0.118	0.141
R_2	0.010	0.056	0.068	0.069	0.073	0.075	0.079	0.080
75.0 °C in CCl_4 (c = 0.353; p = 0.004)								
Reaction time/s	0	7 200	14 400	21 600	28 800	396 000	50 400	61 200
R_1	0.007	0.021	0.040	0.055	0.069	0.100	0.125	0.146
R_2	0.053	0.061	0.068	p.071	0.081	0.077	0.080	0.081
80.0 °C in CCl_4 (c = 0.0353; p = 0.003)								
Reaction time/s	0	3 600	7 200	10 800	14 400	18 800	28 800	
R_1	0.005	0.020	0.034	0.040	0.068	0.083	0.128	
R_2	0.017	0.058	0.065	0.066	0.073	0.075	0.079	
80 °C in octane (c = 0.353; p = 0.004)								
Reaction time/s	0	3 305	6 000	9 000	120 000	15 030	180 000	
R_1	0.007	0.019	0.029	0.042	0.053	0.066	0.078	
R_2	0.024	0.056	0.062	0.066	0.069	0.070	0.072	
80 °C in Nujol (c = 0.351; p = 0.005)								
Reaction time/s	0	6 000	12 000	18 000	24 000	30 000	36 000	
R_1	0.010	0.054	0.0102	0.140	0.176	0.208	0.248	
R_2	0.048	0.076	0.082	0.086	0.089	0.093	0.095	

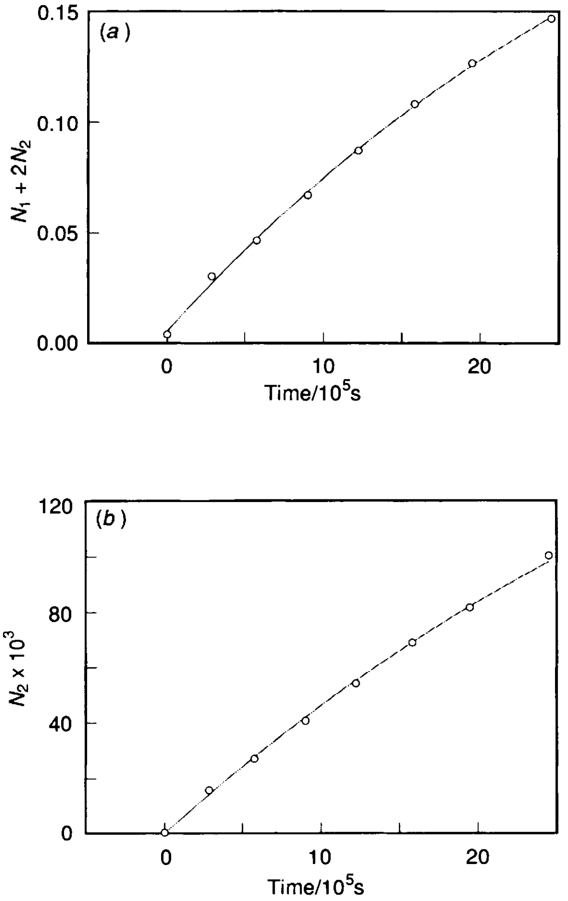

Fig. 3 (*a*) Curve fitting of the experimentally observed values of (N_2 + $2N_2$) at 65 °C to eqn. (7). (*b*) Curve fitting of the experimentally observed values of N_2 at 65 °C to eqn. (8). Results are listed in Table 5, together with the ones obtained at different temperatures.

turning the L-tube. After stirring for 20 min, the reaction flask was cooled with a liquid nitrogen bath and the oxygen gas evolved was transferred into a gas sampler by a Teppler pump. The oxygen gas was introduced into the mass spectrometer to record peaks of m/z 32, 34 and 36. R_1 and R_2 listed in Table 6 were computed from the mass spectral data according to eqns. (5) and (6). Rate constants for both total (k_{ts}) and random (k_{rs}) scramblings were computed by putting values of R_1 and R_2 into eqns. (7) and (8) by a non-linear least-squares program. Plots of the experimental values of R_1 and R_2 were superimposed excellently with the simulation curves for R_1 and R_2 figures based on experimentally observed values of k_{ts} and k_{rs} (Fig. 3), revealing that the data obtained in these ^{18}O-tracer experiments are precise. Fig. 3 shows a typical example.

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