Thermal decomposition of diacyl peroxide. Part 11.[1] ^{18}O-Scrambling in carbonyl-^{18}O-labelled phthaloyl peroxide,† a cyclic Case III diacyl peroxide. Extremely large return of unescapable acyloxyl radical pair

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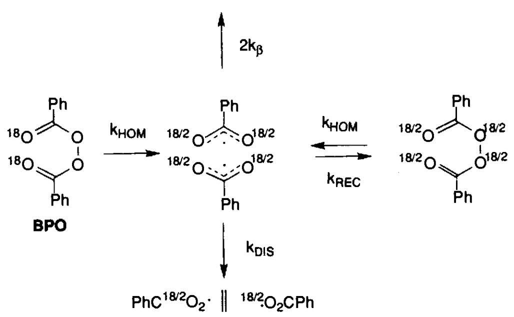
^{18}O-Scrambling in carbonyl-^{18}O-labelled phthaloyl peroxide, a cyclic Case III diacyl peroxide, proceeds 42 times faster than its decomposition at 80 °C. This is the only diacyl peroxide for which ^{18}O-scrambling takes place faster than the decomposition. The activation parameters have been found to be $\Delta_d H^{\ddagger} = 33.4 \pm 0.7$ kcal mol^{-1} and $\Delta_d S^{\ddagger} = 5.9 \pm 1.9$ cal mol^{-1} K^{-1} for decomposition and $\Delta_s H^{\ddagger} = 31.9 \pm 0.9$ kcal mol^{-1} and $\Delta_s S^{\ddagger} = 9.5 \pm 2.6$ cal mol^{-1} K^{-1} for ^{18}O-scrambling. The results are best explained in terms of 97.6% of return of the phthaloyloxyl radical intermediate which is generated by homolysis of the O–O bond of the peroxide affording the ^{18}O-scrambled peroxide. Based on this mechanism, the transition state for degradation of the phthaloyloxyl radical intermediate is estimated to be 1.5 kcal mol^{-1} greater than the recombination. Comparison of the kinetic data for phthaloyl peroxide with those for benzoyl peroxide reported by Martin and Hargis reveals that the extreme thermal stability of phthaloyl peroxide is not due to its cyclic structure which may hinder the O–O stretching vibration, but attributed to the facile phthaloyloxyl radical return. These observations clearly support our postulate concerning the structural effect on the ^{18}O-scrambling of diacyl peroxide which indicates that the recombination of the aroyloxyl radical pair has to overcome a substantial activation energy barrier while a very small activation energy is necessary for aliphatic ones. The present kinetic data are discussed in comparison with those for the Cope rearrangement of 1,4-bis(dideuteriomethylidene)cyclohexane.

Diacyl peroxides are heteroatom derivatives of hexa-1,5-diene, namely, 1,3,4,6-tetraoxahexa-1,5-diene derivatives.[1] The mechanism of the ^{18}O-scrambling of the ^{18}O-labelled diacyl peroxides,[1–4] *i.e.* the tetraoxa-Cope rearrangement, is an interesting problem in connection with the mechanism of the Cope rearrangement of hexa-1,5-diene derivatives in which both the concerted[5] and the stepwise mechanism *via* cyclohexane-1,4-diyls or biradicalloids[6] have been proposed.



Scheme 1

Previously, since reactivities of diacyl peroxides (RCO–OO–COR′) are highly dependent on the structure of R and R′, we classified diacyl peroxides into the following three cases, *i.e.* Case I, R,R′: alkyl; Case II, R: alkyl, R′: aryl; Case III, R,R′: aryl.[4] In the preceding paper,[1] the ^{18}O-scrambling of cyclopropanecarbonyl peroxide, a Case I diacyl peroxide, has been shown to proceed by recombination of an intimate cyclopropanecarbonyl radical pair rather than [3,3]sigmatropy. According to this mechanism, the rate constants for decomposition (k_d) and ^{18}O-scrambling (k_{ts}) and the fraction of cage return of the acyloxyl radical pair (f_r) are expressed by eqns. (1)–(3) in terms of rate constants of the elementary rate processes. Therefore, the rate constant (k_{HOM}) for O–O bond homolysis is a sum of k_{ts} and k_d [eqn. (4)].

$$k_d = k_{HOM}(k_{DIS} + 2k_\beta)/(4k_{REC} + k_{DIS} + 2k_\beta) \quad (1)$$

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

$$f_r = 4k_{REC}/(4k_{REC} + k_{DIS} + 2k_\beta) \quad (3)$$

$$k_{HOM} = k_{ts} + k_d \quad (4)$$

The f_r value for a usual Case I diacyl peroxide is smaller than 0.5, since the rate of decarboxylation of the acyloxyl radical pair intermediate (k_β) is greater than that for recombination (k_{REC}). However, the value of f_r for the benzoyloxyl radical pair generated in the thermolysis of benzoyl peroxide (a typical Case III diacyl peroxide) in solvents is known to be quite low even though decarboxylation of the benzoyloxyl radical is very slow and the radical too long-lived to have much chance to

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† Phthaloyl peroxide = 2,3-benzodioxan-1,4-dione.

Table 1 Effect of initial concentration of PPO on rate of decomposition at 80 °C[a]

$[PPO]_0$/mmol dm^{-3}	0.010 mol dm^{-3} $Na_2S_2O_3$ titre[b]/cm^3	$k_d/10^{-7}$ s^{-1} [c]
10.0	6.69 ± 0.01	3.41 ± 0.01
2.00	6.78 ± 0.29	3.21 ± 0.14
1.25	6.66 ± 0.04	3.46 ± 0.02
1.00	6.69 ± 0.01	3.41 ± 0.01

[a] Reaction time: 211.5 h. [b] Each reaction tube contained the same amount of PPO (titre at time zero = 8.67 ± 0.05 cm^3). [c] Apparent first-order rate constant for the decomposition calculated by the one point kinetics.

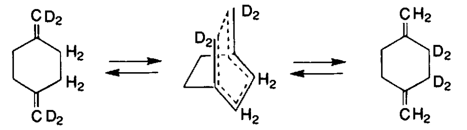
Table 2 First-order rate constants and activation parameters for decomposition and ^{18}O-scrambling of PPO in CCl_4[a]

Temp./°C	$k_d/10^{-6}$ s^{-1}	$k_s/10^{-6}$ s^{-1}
60.0		0.863 ± 0.041
70.0		3.89 ± 0.10
80.0	0.312 ± 0.032	13.0 ± 0.3
90.0		53.6 ± 0.8
100.0	4.17 ± 0.06	
110.0	11.9 ± 0.8	
120.0	47.5 ± 1.2	
130.0	126 ± 8.6	
$\Delta H^{\ddagger}$/kcal mol^{-1}	33.4 ± 0.7	31.9 ± 0.9
$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	5.9 ± 1.9	9.5 ± 2.6

[a] $[PPO]_0$ = 5 mmol dm^{-3}.

recombine back to the peroxide.[2b] This was rationalized in terms of the greater activation energy barrier for the recombination of the benzoyloxyl radical pair than that for the dissociation of the radical pair out of the cage in a usual solvent based on the mechanism shown in Scheme 1.[1,4] According to this picture, the f_r value of a cyclic Case III diacyl peroxide which gives an unescapable acyloxyl radical pair linked by a covalent bond should be nearly 1, since the activation energy for the decarboxylation of aroyloxyl radical is relatively large and hence the recombination of the radical pair may become the fastest process of the unescapable aroyloxyl radical pair. Phthaloyl peroxide (PPO) may be such a particular Case III diacyl peroxide, which affords an intramolecular aroyloxyl radical pair. However, Greene reported that ^{18}O-scrambling of the carbonyl-^{18}O-labelled PPO could not be detected in the peroxide recovered after heating the peroxide in CCl_4 for 96 h at 80 °C.[7] This earlier observation rules out our postulate. However, Greene's observation was based on the indirect experiment for the ^{18}O-scrambling of PPO.[7] Therefore, we have re-examined the possibility of a large f_r value in the thermolysis of ^{18}O-labelled PPO to support our postulate by direct observation of ^{18}O-content of the peroxidic oxygens of the peroxides recovered after partial decomposition.

The ^{18}O-scrambling in PPO is also interesting in connection with the deuterium scrambling between C-1 and C-3 or C-3 and C-6 by the Cope rearrangement of 1,4-bis(dideuteriomethylidene)cyclohexane and its derivatives, since the transition state of the Cope rearrangement involves a substantial extent of the new bond between the two methylidene groups, although the alkenic terminal carbon atoms which are going to make a new bond are far from each other in the ground state (Scheme 2).[8]



Scheme 2

Results

Kinetics of thermal decomposition of phthaloyl peroxide (PPO)

Decomposition of peroxides has been carried out in CCl_4 in degassed sealed Pyrex glass tubes. The kinetics of decomposition were determined by the routine iodometric titration method.[4] Since PPO is known to be quite sensitive to the induced decomposition,[7] the initial rate of decomposition was examined to check the induced decomposition with solutions of various concentrations (Table 1). Tubes containing solutions of 8 μmol of PPO in CCl_4 of various PPO concentrations (0.001–0.01 mol dm^{-3}) were heated at 80 °C for 211.5 h and the amount of remaining PPO in each tube was determined iodometrically. As shown in Table 1, 0.005 mol dm^{-3} is low enough to determine the unimolecular rate constant for PPO (k_d). The kinetic data for decomposition of PPO obtained at various temperatures are summarized in Table 2 together with activation parameters.

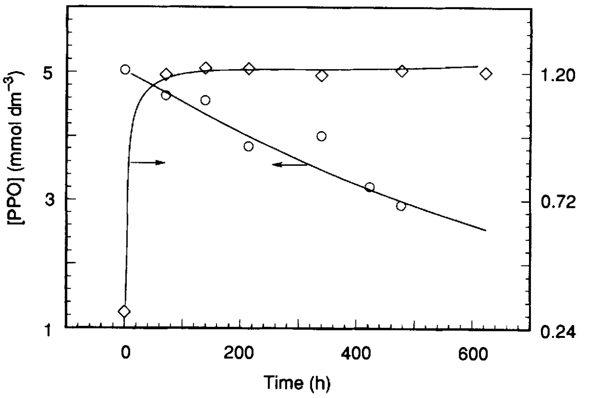
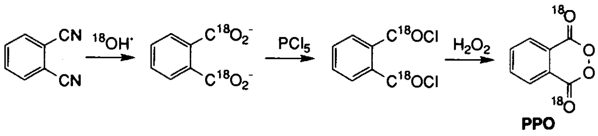


Fig. 1 Preliminary test for oxygen scrambling in PPO at 80 °C in CCl_4. Circles represent concentration of PPO. Squares represent ^{18}O-content in the dioxygen gas derived from the peroxidic oxygen atoms of recovered PPO.

Kinetics of ^{18}O-scrambling

Carbonyl-^{18}O-labelled PPO was prepared by the synthetic route shown in Scheme 3. The thermolysis of carbonyl-^{18}O-labelled PPO was carried out under the same conditions applied to the determination of kinetics of decomposition. The two peroxidic oxygen atoms of PPO recovered after heating were converted to oxygen gas by sequential treatment with sodium methoxide, sulfuric acid and then with Ce^{4+} in a vacuum line.[1] The dioxygen gas obtained was subjected to MS analysis to record peaks of *m*/*z* 32, 34 and 36. At the beginning, [^{18}O]PPO was heated until its half-life of PPO, and the MS peak height ratios of *m*/*z* 34/32 of the dioxygen recovered after various reaction times are illustrated in Fig. 1.



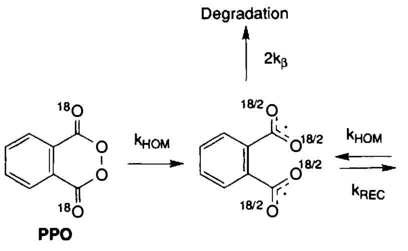
Scheme 3

Even after 70.5 h, after which only 9% of PPO had decomposed, the ^{18}O label was completely scrambled in the four oxygen atoms of the PPO revealing that ^{18}O-scrambling of PPO proceeds one order of magnitude faster than the decomposition. This was further confirmed by using PPO with a high content of ^{18}O. When [^{18}O]PPO, synthesized according to Scheme 3 using water containing 11% ^{18}O, was heated at 80 °C for 5 days, the MS peak height ratios of the dioxygen gas derived from the peroxidic oxygens of the recovered peroxide were found to be *m*/*z* 34/32 = 0.109 and *m*/*z* 36/34 = 0.028. These experimental values are identical to the value calculated by the mechanism shown in Scheme 4; *i.e.* ^{18}O-scrambling

Table 3 Comparison of the kinetic behaviour of cyclic Case III diacyl peroxide (PPO) with that of the acyclic one (BPO)

Peroxide	Solvent	$k_d/10^{-5}\ s^{-1}$	$k_{ts}/10^{-5}\ s^{-1}$	$k_{HOM}/10^{-5}\ s^{-1}$	f_r
PPO	CCl_4	0.0312	1.30	1.33	0.976
BPO (ref. 2*b*)	C_8H_{18}[i]	2.70	0.13	2.83	0.046

occurs *via* the recombination of phthaloyloxyl radical in which the four oxygen atoms are equivalent. Then the rate of ^{18}O-scrambling was determined at various temperatures. Since experiments were carried out by using 2 atom% [^{18}O]PPO, the ^{18}O-content of PPO was not high enough to determine the MS peak height ratio of m/z 36/34 accurately to calculate the rate constant of the random scrambling (k_{rs}). However, sufficiently accurate MS peak height ratios of m/z = 34/32 were obtained to compute the rate constant of the total scrambling (k_{ts}). Based on the mechanism in Scheme 4, f_r was calculated from k_d and k_{ts} at 80 °C to be 0.976, *i.e.* 97.6% of phthaloyloxyl radical intermediates recombine to PPO. Among the many diacyl peroxides that we have encountered, PPO is the only diacyl peroxide in which ^{18}O-scrambling takes place faster than the decomposition.



Scheme 4

Discussion

The extremely large f_r value for the thermolysis of PPO is considered to support our postulate that the recombination of an unescapable acyloxyl radical pair generated from the O–O bond homolysis of a Case III diacyl peroxide possessing cyclic peroxide structure greatly predominates over the degradation of the acyloxyl radical pair. Thus, these observations may be strong evidence for verifying our postulate concerning the structural effect on the fates of acyloxyl radical pair generated in the thermal decomposition of Case I, II and III diacyl peroxides.[4]

The comparison of kinetic data for this particular Case III diacyl peroxide with those for BPO, *i.e.* the usual Case III peroxide, may be helpful in characterizing the nature of the Case III acyloxyl radical pair reported by Martin and Hargis.[2b] The sum of experimentally obtained values of k_d and k_{ts} for PPO gives k_{HOM} [from eqn. (4)] in CCl_4 at 80 °C to be $1.33 \times 10^{-5}\ s^{-1}$. Similarly k_{HOM} for BPO in isooctane at 80 °C was calculated to be $2.83 \times 10^{-5}\ s^{-1}$ from the kinetic data of Martin and Hargis.[2b] Although acyclic peroxide (BPO) decomposes 87 times more readily than the cyclic one (PPO), the rate of O–O bond homolysis of BPO is only 2.1 times greater than that of PPO (Table 3). Therefore, the thermal stability of PPO in comparison with BPO cannot be attributed to the cyclic structure of PPO in which the O–O bond stretching is hindered, but to the lack of the diffusion process of two acyloxyl radical groups which is usually the fastest process in the fates of a benzoyloxyl radical pair formed from BPO in a solvent cage.

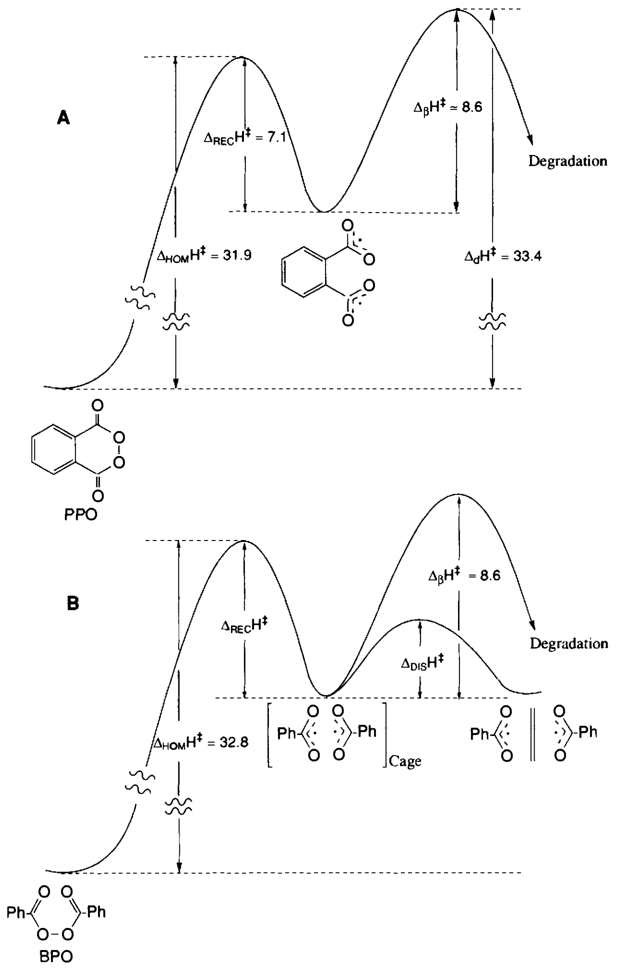
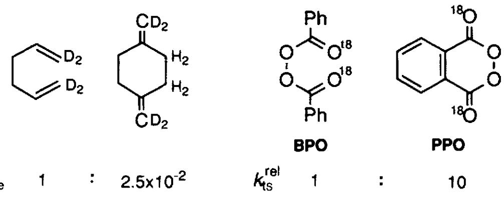


Fig. 2 Potential energy surfaces for thermolyses of PPO (**A**) and BPO (**B**). Values of activation enthalpies are shown in kcal mol^{-1}.

Since $k_{ts} \gg k_d$ for PPO, the enthalpy of activation for the homolysis of the O–O bond ($\Delta_{HOM}H^\ddagger$) of PPO is roughly equal to the enthalpy of activation for the ^{18}O-scrambling ($\Delta_sH^\ddagger$) (Fig. 2). On the other hand, since $k_{ts} \ll k_d$ for BPO, $\Delta_{HOM}H^\ddagger = \Delta_dH^\ddagger$ for thermolysis of BPO. The difference in the enthalpies of activation for the degradation ($\Delta_\beta H^\ddagger$) and for the recombination of the phthaloyloxyl radical ($\Delta_{REC}H^\ddagger$) can be calculated to be only 1.5 kcal mol^{-1} from the data in Table 3 and the relationship of $\Delta_dH^\ddagger - \Delta_sH^\ddagger = \Delta_\beta H^\ddagger - \Delta_{REC}H^\ddagger$ for the thermolysis of PPO. Development of experimental techniques has allowed new aroyloxyl chemistry to be discovered. The rate for decarboxylation (k_β) of the benzoyloxyl radical determined in the past 10 years[9,10] is much greater than the value estimated earlier by Bevington *et al.* based on their indirect method involving trapping of benzoyloxyl radicals thermally generated during the polymerization of styrene initiated by BPO at 60 and 80 °C.[11] Yamauchi *et al.* succeeded in measuring directly k_β for the benzoyloxyl radical generated by the laser flash photolysis of BPO in CCl_4 at −14 to 20 °C and determined $\Delta_\beta H^\ddagger$ to be 5 kcal mol^{-1}.[9] Later, Chateauneuf *et al.* measured values of k_β for benzoyloxyl radicals generated by laser flash photolysis of BPO in CCl_4 in a temperature range of −21 to 53 °C and determined $\Delta_\beta H^\ddagger$ to be 8.6 kcal mol^{-1}.[10c] There is substantial discrepancy between the values of $\Delta_\beta H^\ddagger$ reported by these two groups. The latter value seems to be more reliable since the temperature range in the latter measurement is much wider than in the former experiment. If the value of $\Delta_\beta H^\ddagger$ for the phthaloyloxyl radical in the present experiment is assumed to be similar to $\Delta_\beta H^\ddagger$ for the benzoyloxyl radical, $\Delta_{REC}H^\ddagger$ of phthaloyloxyl radical is calculated to be *ca.* 7.1 kcal mol^{-1}. Although $\Delta_sH^\ddagger$ for BPO has not been determined, $\Delta_{REC}H^\ddagger$ would be similar to that for the phthaloyloxyl radical. This substantial activation energy barrier (7.1 kcal mol^{-1}) observed for the recombining benzoyloxyl radical pair answers the question as to why the k_d of value BPO is unexpectedly inert to the change in the viscosity of the medium,[12] although BPO is really a one-bond fission initiator.[13]

The enthalpy of activation for the Cope rearrangement of 1,1,6,6-tetradeuteriohexa-1,5-diene is 24.1 kcal mol^{-1} (chair form transition state)[6a] or 17.5 kcal mol^{-1} (boat form transition state)[14] both of which are less than that for the C-3–C-4 bond homolysis affording the allyl radical pair.[6a] This enthalpy difference, $\Delta\Delta H^{\ddagger}_{\text{(homolysis–rearrangement)}}$, is caused mainly by the partial new bond formation in the transition state of the rearrangement between C-1 and C-6 regardless of the mechanism. The value of $\Delta\Delta H^{\ddagger}_{\text{(homolysis–rearrangement)}}$ for the Cope rearrangement of 1,4-bis(dideuteriomethylidene)-cyclohexane is still substantial (13 kcal mol^{-1}) revealing that the reaction is still the new bond making type rearrangement (Scheme 2).[8] However, the possibility that the transition state for ^{18}O-scrambling is stabilized by formation of a partial new bond in the same manner as the Cope rearrangement of dienes may be ruled out for the following reasons. (*a*) The original carbonyl-^{18}O-labels are completely scrambled into four oxygen atoms of PPO. (*b*) The Cope rearrangement of acyclic diene, 1,1,6,6-tetradeuteriohexa-1,5-diene, proceeds 97 times faster than the cyclic one, 1,4-bis(dideuteriomethylidene)cyclohexane, at 300 °C.[8] However, k_{ts} of the acyclic Case III peroxide, BPO, is $0.1k_{ts}$ the value of the cyclic one, PPO, as shown in Scheme 5. These opposite structure effects observed in these two rearrangements follow the same trend as the rate of the Cope rearrangement; the rate increases in the order of Case I < Case II < Case III, while k_{ts} of diacyl peroxide increases in the order of Case III < Case II < Case I. These opposite structure effects in the two reactions suggest that the ^{18}O-scrambling in the diacyl peroxide is a bond-breaking type rearrangement in contrast to the Cope rearrangement that is a bond-forming type rearrangement.



Scheme 5 Comparison of the Cope rearrangements with the tetraoxa-Cope rearrangements

Ground state of the benzoyloxyl radical is known to be the σ-radical in the $^2B_2$ state,[9,10c,15] while the π-radical is an excited state, $^2A_2$.[15] If the ground state of the phthaloyloxyl radical is also a σ-radical, the π-system in the σ-phthaloyloxyl radical accommodates eight electrons, as shown in Fig. 3, and hence no stabilization can be expected. Although the π-system in the π-phthaloyloxyl radical accommodates six electrons to possess aromaticity, the π-radical is an excited state of a single acyloxyl radical and hence in this case no stabilization would be expected.‡

Experimental

Carbon tetrachloride (extra pure grade, Wako) was washed with aqueous potassium carbonate solution, dried (K_2CO_3) and distilled through a fractional column, bp 77 °C. Mass spectra were recorded on an Hitachi RMU-6MG mass spectrometer. IR spectra were recorded on a Hitachi 260–50 spectrometer.

Synthesis of ^{18}O-labelled phthaloyl chloride

Phthalonitrile (1.73 g) and ^{18}O-enriched water (1.6–11 atom%) were added to sodium methoxide solution, prepared from 1.6 g of sodium and 30 cm^3 of absolute methanol and refluxed for 10 days. Methanol was evaporated and the residue was dissolved in water. The water solution was washed with diethyl ether and acidified with hydrochloric acid. Crystals of phthalic acid formed were collected and dried (2.12 g, mp 228–230 °C). A mixture of ^{18}O-labelled phthalic acid (2.12 g) and 6.62 g of phosphorus pentachloride was heated at 150 °C for 15 h and distilled. The fraction at bp 130–133 °C/9–10 Torr gave a colourless oil of ^{18}O-labelled phthaloyl chloride (2.30 g).

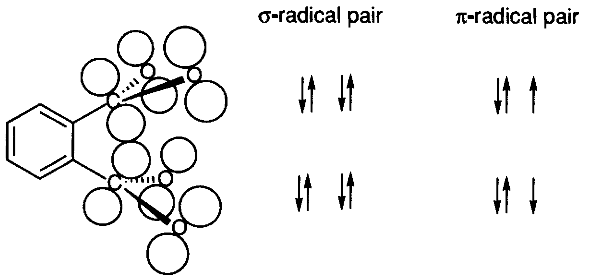


Fig. 3 Number of π-electrons in acyloxyl moieties of phthaloyloxyl radicals in the states of intramolecular σ-radical pair and π-radical pair

Synthesis[16] of carbonyl-^{18}O-labelled PPO

A solution of 15 g of $Na_2PO_4{\cdot}12H_2O$ and 7.5 g of $NaH_2PO_4{\cdot}2H_2O$ in 200 cm^3 of water was placed in a 500 cm^3 three-necked flask equipped with a mechanical stirrer and cooled to 5 °C in an ice bath. Then, sodium peroxide (1.2 g) was added to the stirred solution, to which 2.3 g of phthaloyl chloride in 160 cm^3 of $CHCl_3$ was added at 0–5 °C.[16] Stirring was continued for 4 h at 0–5 °C. The organic layer was separated, washed with water, dilute $NaHCO_3$ solution and then water at room temperature and dried (Na_2SO_4). The solution was filtered and evaporated to near dryness under reduced pressure at below room temperature to obtain white crystals of PPO, which upon recrystallization from CCl_4 afforded colourless needles of pure ^{18}O-labelled PPO (0.48 g); $\nu(CCl_4)$/cm^{-1} 1768 (C=O, strong), 1285, 1092, 1040 and 690.

Kinetics of decomposition of peroxides

10 cm^3 of 0.005 mol dm^3 peroxide solution in CCl_4 was pipetted into eight Pyrex glass tubes, which were washed first with dilute HF solution, subsequently by distilled water, dried in an oven and cooled before use. Each of the charged tubes was connected to the vacuum line, degassed by freeze-pumping–thaw cycles twice and sealed. All the tubes were immersed in a thermostatted bath within ±0.1 °C. The first tube was picked up after 5 min and suddenly cooled in a dry ice–acetone bath ($t = 0$). The remaining tubes were picked after appropriate intervals and cooled. The recovered tube was opened and the amount of undecomposed peroxide was determined by iodometry as described elsewhere.[4]

Kinetics of ^{18}O-scrambling of PPO

Thermolysis of the [^{18}O]PPO was carried out following the same procedure as was used for determining the kinetics of decomposition. Each tube was charged with 0.005 mol dm^{-3} [^{18}O]PPO so as to leave 1.5 μmol of the undecomposed peroxide after an appropriate reaction time. The recovered peroxide was treated with $NaOCH_3$, H_2SO_4 and $Ce(SO_4)_2$ to convert the peroxidic oxygen atoms of PPO into dioxygen which was subjected to MS analysis as mentioned previously.[1]

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‡ If the energy of the bonding interaction in the π-radical pair shown in Fig. 3 is greater than the excitation energy of the [$^2B_2$] state to the [$^2A_2$] state, the π-radical pair in Fig. 3 may contribute partly to the ^{18}O-scrambling of PPO.

References

1 For Part 10, see K. Fujimori, Y. Hirose and S. Oae, *J. Chem. Soc., Perkin Trans. 2*, preceding paper.

2 (*a*) J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.*, 1967, **89**, 6904; (*b*) J. C. Martin and J. H. Hargis, *J. Am. Chem. Soc.*, 1969, **91**, 5399.

3 (*a*) M. J. Goldstein and H. A. Judson, *J. Am. Chem. Soc.*, 1970, **92**, 4119; (*b*) M. J. Goldstein and W. A. Haiby, *J. Am. Chem. Soc.*, 1974, **96**, 7358.

4 K. Fujimori and S. Oae, *Tetrahedron*, 1973, **29**, 65.

5 (*a*) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**, 4389; (*b*) J. J. Gajewski, *Acc. Chem. Res.*, 1980, **13**, 142.

6 (*a*) W. v. E. Doering, V. G. Toscano and G. H. Beasley, *Tetrahedron*, 1971, **17**, 299; (*b*) W. R. Roth, H.-W. Lennartz, W. v. E. Doering, C. A. Guyton and T. Kitagawa, *J. Am. Chem. Soc.*, 1990, **112**, 1722; (*c*) M. J. S. Dewar, G. P. Ford, M. L. Mckee, H. S. Rzepa and L. E. Wade, *J. Am. Chem. Soc.*, 1977, **99**, 5069; M. J. S. Dewar and C. Jie, *Acc. Chem. Res.*, 1992, **25**, 537.

7 (*a*) F. D. Greene, *J. Am. Chem. Soc.*, 1956, **78**, 2246; (*b*) F. D. Greene, *J. Am. Chem. Soc.*, 1959, **81**, 1503.

8 W. v. E. Doering and C. A. Troise, *J. Am. Chem. Soc.*, 1985, **107**, 5739.

9 S. Yamauchi, N. Hirota, N. Takahara, H. Sakuragi and K. Tokumaru, *J. Am. Chem. Soc.*, 1985, **107**, 5021; H. Misawa, K. Sawabe, S. Takahara, H. Sakuragi and K. Tokumaru, *Chem. Lett.*, 1988, 357.

10 (*a*) J. Chateauneuf, J. Luztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1987, **109**, 897; (*b*) J. Chateauneuf, J. Luztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 2877; (*c*) J. Chateauneuf, J. Luztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 2866.

11 J. C. Bevington, J. Toole and E. Trossarelli, *Trans. Faraday Soc.*, 1958, **54**, 863.

12 W. A. Pryor and K. Smith, *J. Am. Chem. Soc.*, 1979, **92**, 5403.

13 (*a*) G. S. Hammond and L. M. Soffer, *J. Am. Chem. Soc.*, 1950, **72**, 4771; (*b*) E. G. Janzen, C. A. Evans and Y. Nishi, *J. Am. Chem. Soc.*, 1972, **94**, 8236; (*c*) H. Sakuragi and K. Tokumaru, *Chem. Lett.*, 1988, 357.

14 M. J. Goldstein and M. S. Benzon, *J. Am. Chem. Soc.*, 1972, **94**, 7147.

15 (*a*) E. S. Feller, W. T. Huyser, W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, 1983, **105**, 1459; (*b*) A. D. McLean, B. H. Lengsfield III, J. Pacansky and Y. Ellinger, *J. Chem. Phys.*, 1985, **83**, 3567.

16 K. E. Russel, *Can. J. Chem.*, 1960, **38**, 1600.

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