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Structural effects on the reactivity for decarboxylation and absorption of aroyloxyl radicals generated by laser photolysis of diaroyl peroxides

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Abstract

A profile of the effect of the structure of aroyloxyl radicals (generated by laser flash photolysis of various diaroyl peroxides in acetonitrile and carbon tetrachloride) on the reactivity for decarboxylation and absorption is presented by classification of the radicals into four groups.

Keywords: Decarboxylation; Absorption; Aroyloxyl radicals; Laser photolysis; Diaroyl peroxides

1. Introduction

Diaroyl peroxides have long been used as initiators of radical polymerizations [1,2]. On thermolysis or photolysis, the peroxides dissociate into aroyloxyl radicals, which subsequently decarboxylate to give aryl radicals or react with substrates, such as vinyl monomers (M), as shown in Scheme 1. The rate constants for decarboxylation of the aroyloxyl radicals and their reactions with substrates have been estimated by employing a rotating sector procedure or by assuming the rate constants for addition of the aroyloxyl radicals to the monomers [3].

During the course of an investigation into the photolysis of diaroyl peroxides [4], we succeeded [5,6], for the first time, in observing directly benzoyloxyl radicals with a time-resolved electron paramagnetic resonance (TREPR) method on photodecomposition of several dibenzoyl peroxides, such as bis(4-methoxybenzoyl) peroxide (4-MeOBPO), bis(4-chlorobenzoyl) peroxide (4-ClBPO) and dibenzoyl peroxide (BPO), in carbon tetrachloride at room temperature. The absolute values of the lifetimes of the benzoyloxyl radicals and the activation parameters for decarboxylation were obtained and found to be quite different from those often quoted.

$$\mathrm{ArCO_2OCOAr} \longrightarrow \mathrm{2ArCO_2\cdot}$$
$$\mathrm{ArCO_2\cdot} \longrightarrow \mathrm{Ar\cdot + CO_2}$$
$$\mathrm{ArCO_2\cdot + M} \longrightarrow \mathrm{ArCO_2M\cdot}$$

Scheme 1.

The above work led Ingold and coworkers [7,8] and ourselves [9] to pursue aroyloxyl radicals by transient absorption spectroscopy. The kinetic characteristics of the aroyloxyl radicals examined were in excellent agreement with those obtained by the TREPR method. Subsequently, we investigated the behaviour of various aroyloxyl radicals using transient absorption spectroscopy together with product studies [10–13]. In this paper, we aim to determine the effect of structure on the reactivity for decarboxylation and spectra of a series of aroyloxyl radicals by classifying them into four groups. These groups are defined particularly in terms of the effect of steric congestion around the carboxyl radical centre, which leads to twisting of the carboxyl moiety from the aromatic ring, and the effect of the introduction of naphthalene, a larger aromatic ring, instead of the benzene ring in benzoyloxyl radicals.

2. Spectroscopic characteristics of aroyloxyl radicals

Figs. 1–6 depict the transient absorption spectra observed on 308 nm laser excitation of diaroyl peroxides in deaerated acetonitrile and carbon tetrachloride solutions. The spectra observed for the diaroyl peroxides [10–13], with the exception of bis(2-ethylbenzoyl) peroxide (2-EtBPO) and bis(2-benzylbenzoyl) peroxide (2-PhCH$_2$BPO) [11,13], show absorption profiles similar to those of 4-MeOC$_6$H$_4$CO$_2$$^\cdot$ and C$_6$H$_5$CO$_2$$^\cdot$ [9]; the absorption increases in intensity from the 500–600 nm region to the longer wavelength region, but the absorption maxima are not observed below 800 nm in most

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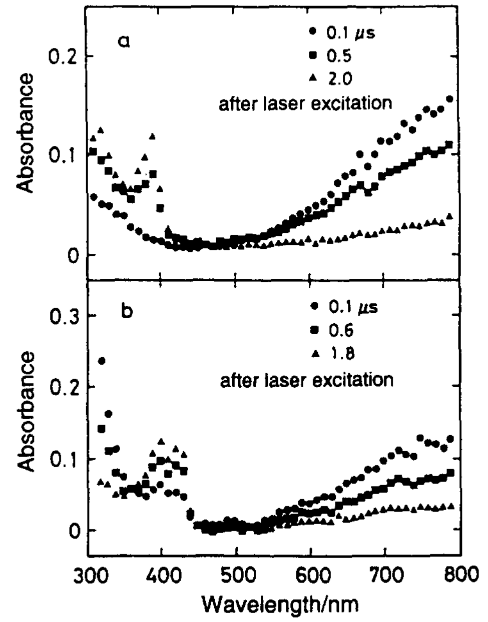


Fig. 1. Transient absorption spectra observed on laser excitation of bis(4-methoxybenzoyl) peroxide (4-MeOBPO) (a) and dibenzoyl peroxide (BPO) (b) in acetonitrile.

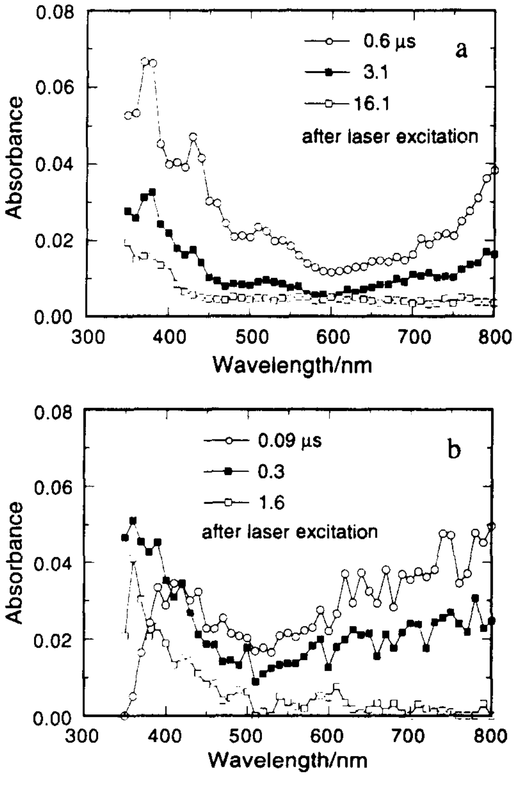


Fig. 2. Transient absorption spectra observed on laser excitation of bis(1-naphthoyl) peroxide (1-NPO) (a) and bis(2-naphthoyl) peroxide (2-NPO) (b) in carbon tetrachloride.

cases. The observed absorptions can be safely assigned to the corresponding aroyloxyl radicals, $ArCO_2^{\cdot}$, since they appear instantaneously after the laser pulse, and are unaffected by the presence of oxygen. Most of these absorptions simply decay by first-order kinetics via decarboxylation. Table 1 lists the rate constants at ambient temperature, activation energies and frequency factors for the decay of the aroyloxyl radicals in acetonitrile and carbon tetrachloride.

The spectra for bis(2,6-dimethylbenzoyl) peroxide (2,6-Me_2BPO), bis(2,6-dichlorobenzoyl) peroxide (2,6-Cl_2BPO) and bis(2,4,6-trimethylbenzoyl) peroxide (2,4,6-Me_3BPO) show absorption with a maximum around 700 nm and a shorter wavelength component around 450 nm [12]; these spectra are clearly shifted to shorter wavelengths compared with those of the other unsubstituted and monosubstituted benzoyloxyl radicals. The presence of two methyl groups or two chlorine atoms at the ortho positions may induce the twisting of the carboxyl group from the aromatic ring plane.

The nature of the long-wavelength absorption of many aroyloxyl radicals is not yet fully understood. However, if the aroyloxyl radicals exist as σ radicals, the allowed transition must take place between the σ orbitals in the carboxyl plane, from a $^2B_2$ state to a $^2A_1$ state [6,8,16,17]. On twisting, these σ orbitals can interact with the π orbitals in the aromatic ring [18].

The observed shift of the absorption maximum to about 700 nm from the longer wavelength region on substitution of two methyl groups or two chlorine atoms at the 2 and 6 positions suggests that the above interaction results in an increase in the energy difference between the two σ states. The present result may be similar to the spectral features of

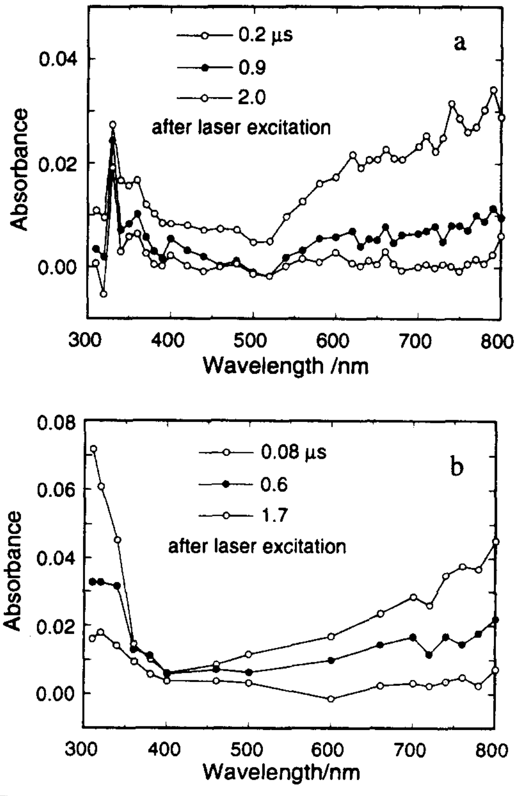


Fig. 3. Transient absorption spectra observed on laser excitation of bis(2-methoxybenzoyl) peroxide (2-MeOBPO) (a) and bis(2-chlorobenzoyl) peroxide (2-ClBPO) (b) in carbon tetrachloride.

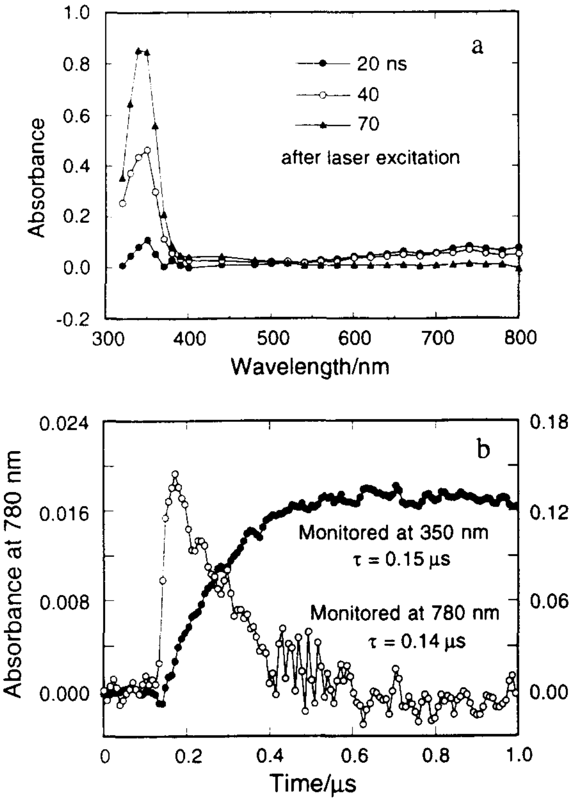


Fig. 4. Transient absorption spectra (a) and time profiles (b) of the transient absorption monitored at 780 and 350 nm on 308 nm laser excitation of bis(2-methylbenzoyl) peroxide (2-MeBPO) in acetonitrile under argon at −40 °C.

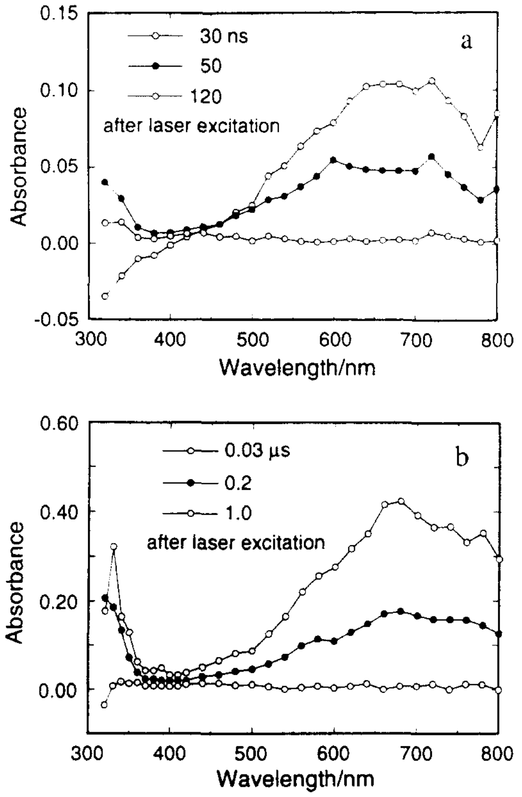


Fig. 5. Transient absorption spectra obtained on 308 nm laser excitation of bis(2,6-dimethylbenzoyl) peroxide (2,6-Me_2BPO) (a) and bis(2,4,6-trimethylbenzoyl) peroxide (2,4,6-Me_3BPO) (b) in acetonitrile.

acetylenecarbonyloxyl radicals, such as tert-$BuC{\equiv}CCO_2^{\cdot}$, in which one of the triple bond π orbitals can interact with the carboxyl σ SOMO [17], and alkoxycarbonyloxyl radicals, such as $CH_3CH_2OCO_2^{\cdot}$, with an absorption maximum around 640 nm [19], in which one of the two non-bonding orbitals on the alkoxy oxygen atom can interact with the σ orbitals of the carboxyl group.

As discussed in the following section, the molar absorption coefficient of $2\text{-}MeC_6H_4CO_2^{\cdot}$ can be estimated to be nearly 1×10^3 M^{-1} cm^{-1} at 780 nm. If $2,6\text{-}Me_2C_6H_3CO_2^{\cdot}$, $2,6\text{-}Cl_2C_6H_3CO_2^{\cdot}$ and $2,4,6\text{-}Me_3C_6H_2CO_2^{\cdot}$ are assumed to have the same molar absorption coefficients at their absorption maxima around 700 nm as that of $2\text{-}MeC_6H_4CO_2^{\cdot}$ at 780 nm, their absorption coefficients are lower than those for strongly allowed π,π^* transitions ($\epsilon_{max} \approx 10^4$ M^{-1} cm^{-1}), higher than those for n,π^* absorptions in aromatic ketones ($\epsilon_{max} \approx 10^1$–$10^2$ M^{-1} cm^{-1}) and comparable with those for π,π^* transitions of medium intensity ($\epsilon_{max} \approx 10^3$ M^{-1} cm^{-1}). The absorption coefficient expected for the $^2B_2$ to $^2A_1$ transition is not yet known. However, the observed absorption certainly seems to be much more intense than a forbidden transition which could result from excitation from the σ SOMO to the π^* orbital of the carboxyl group conjugated with the aromatic ring.

For $1\text{-}NpCO_2^{\cdot}$, the presence of the 1-naphthyl group, which is a larger conjugated group than the benzene ring and

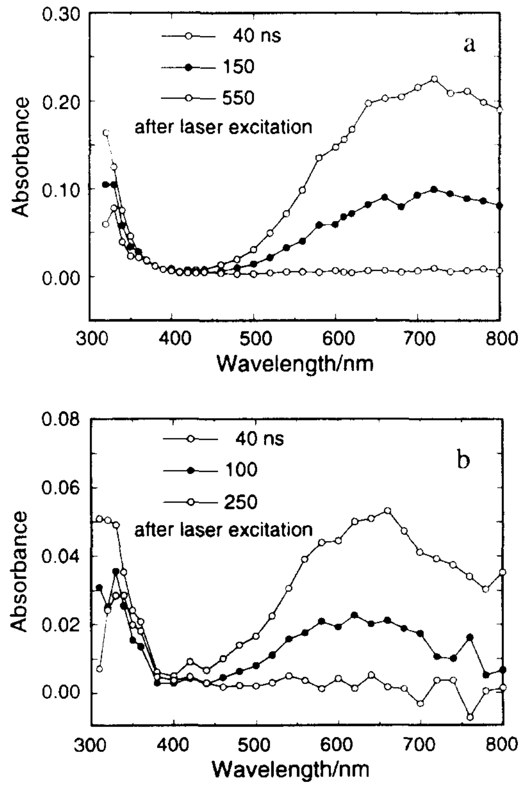


Fig. 6. Transient absorption spectra obtained on 308 nm laser excitation of bis(2,6-dichlorobenzoyl) peroxide (2,6-Cl_2BPO) in acetonitrile (a) and carbon tetrachloride (b).

Table 1
Rate constants (k), activation energies (E_a) and frequency factors (A) for the decay [a] of aroyloxyl radicals ($ArCO_2^{\cdot}$)

$ArCO_2^{\cdot}$	Solvent	[Peroxide]$_0$ (10^{-3} mol dm^{-3})	k [b] (10^6 s^{-1})	E_a (kJ mol^{-1})	log(A(s^{-1}))	Reference
$C_6H_5CO_2^{\cdot}$	CH_3CN	100	5.9	31	12.1	9
	CCl_4		4.5 [d]	24	10.3	6
4-$ClC_6H_4CO_2^{\cdot}$	CH_3CN	38	1.9	39	13.2	9
	CCl_4		1.4 [d]			6
2-$ClC_6H_4CO_2^{\cdot}$	CH_3CN	20	1.5 [e]	36	12.5	12
	CCl_4	20	1.3			12
4-$MeC_6H_4CO_2^{\cdot}$	CH_3CN	25	1.8	39	13.1	14
	CCl_4		2.8 [d]			6
4-$MeOC_6H_4CO_2^{\cdot}$	CCl_4	2.0	0.41 [e]	46	13.6	9
	CH_3CN	10	0.1 [f]			9
2-$MeOC_6H_4CO_2^{\cdot}$	CCl_4	0.7	1.6	37	12.8	15
	CH_3CN	0.2	0.75			15
1-$NpCO_2^{\cdot}$	CH_3CN	0.064	0.32	45	13.5	10
	CCl_4	0.45	5.1	31	12.1	10
2-$NpCO_2^{\cdot}$	CH_3CN	0.94	3.5	38	13.1	10
	CCl_4	0.73	4.0	36	13.0	10
2-$MeC_6H_4CO_2^{\cdot}$ [c]	CH_3CN	50	17	17	10.5	11, 13
2-$MeCH_2C_6H_4CO_2^{\cdot}$ [c]	CH_3CN	50	>50			13
2-$PhCH_2C_6H_4CO_2^{\cdot}$ [c]	CH_3CN	5.0	>50			13
2,6-$Me_2C_6H_3CO_2^{\cdot}$	CH_3CN	5.0	25 [g]	30	12.7	12
	CCl_4	5.0	>50			15
2,6-$Cl_2C_6H_3CO_2^{\cdot}$	CH_3CN	5.0	10	33	12.6	12
	CCl_4	5.0	17			15
2,4,6-$Me_3C_6H_2CO_2^{\cdot}$	CH_3CN	5.0	3.8	35	12.7	12
	CCl_4	5.0	33			15

[a] Decarboxylation unless otherwise noted.
[b] Rate constants at 23 °C unless otherwise noted.
[c] Intramolecular hydrogen-atom transfer.
[d] Results from TREPR.
[e] At 25 °C.
[f] Rate constant for decay of the transient absorption monitored at 720 nm.
[g] At 20 °C.

is undoubtedly twisted from the carboxyl plane, results in absorption at a slightly longer wavelength than $C_6H_5CO_2^{\cdot}$ (towards 800 nm, as shown in Fig. 2).

3. Intramolecular hydrogen-atom transfer in 2-alkylbenzoyloxyl radicals

The benzoyloxyl radicals resulting from bis(2-methylbenzoyl) peroxide (2-MeBPO), 2-EtBPO and 2-$PhCH_2$BPO behave differently from the other benzoyloxyl radicals examined and undergo intramolecular hydrogen-atom transfer from the adjacent alkyl or aralkyl group instead of decarboxylation [11,13]. Thus, as indicated in Fig. 4(a), the absorption observed 20 ns after pulsed laser excitation of 2-MeBPO is mostly attributable to 2-$MeC_6H_4CO_2^{\cdot}$. The absorption decreases in intensity at 500–800 nm with a rate constant of 1.7×10^7 s^{-1} at 23 °C and a new absorption appears around 350 nm; the time constant for the rise at 350 nm is in good agreement with that for the decay at 780 nm as monitored at −40 °C (Fig. 4(b)). The new absorption finally decays by second-order kinetics with an apparent lifetime of the order of 10 μs. The shorter wavelength absorption is assigned to 2-carboxybenzyl radicals, 2-$HOCOC_6H_4CH_2^{\cdot}$, on the basis of the observation of a similar absorption on pulsed laser excitation of 2-bromomethylbenzoic acid, 2-$BrCH_2C_6H_4CO_2H$. The above spectral change can be reasonably attributed to intramolecular hydrogen-atom transfer in the 2-methylbenzoyloxyl radical, giving the benzyl radical with an activation energy of 17 kJ mol^{-1} and a frequency factor of 3.2×10^{10} s^{-1}.

On laser excitation of 2-EtBPO and 2-$PhCH_2$BPO, absorptions attributable to benzyl-type radicals are observed at around 350 nm, but their precursor benzoyloxyl radicals are too short lived to be detected [13]. These observations indicate that the intramolecular hydrogen-atom transfer proceeds with rate constants larger than 5×10^7 s^{-1} in these two kinds of radical. This arises from a generally higher reactivity of the methylene hydrogen atoms in the ethyl and benzyl groups than the methyl hydrogen atoms towards hydrogen abstraction.

The formation of diacid derivatives, (2-$HOCOC_6H_4CHR)_2$ (R≡H, Me and Ph), among the products of irradiation of 2-MeBPO, 2-EtBPO and 2-$PhCH_2$BPO is due to dimerization of the resulting benzyl radicals, 2-$HOCOC_6H_4CHR^{\cdot}$ [13]. These results support intramolecular hydrogen-atom transfer in 2-alkylbenzoyloxyl radicals, as previously proposed by Greene et al. [20] based on the thermal decomposition of 2-MeBPO. However, it is remarkable that the substitution of two methyl groups at both the 2 and 6 positions of the radicals, as in $2,6\text{-}Me_2C_6H_3CO_2^{\cdot}$ and $2,4,6\text{-}Me_3C_6H_2CO_2^{\cdot}$, does not lead to intramolecular hydrogen-atom transfer; they simply decay via decarboxylation [12].

It should be pointed out that the spectral change due to intramolecular hydrogen-atom transfer, observed on excitation of 2-MeBPO, enables the molar absorption coefficient of the benzoyloxyl radicals to be estimated. Inspection of Fig. 4(b) indicates that the decrease in absorbance of $2\text{-}MeC_6H_4CO_2^{\cdot}$ at 780 nm from 0.02 to zero is accompanied by an increase in absorbance of the benzyl radical at 350 nm from zero to 0.14. This corresponds to almost a sevenfold larger change in absorbance than that of the former. Therefore the molar absorption coefficient of $2\text{-}MeC_6H_4CO_2^{\cdot}$ can be estimated to be seven times smaller than that of the benzyl radical. Comparison of the rate constant for decarboxylation of $2\text{-}ClC_6H_4CO_2^{\cdot}$ with the decay rate constant of $2\text{-}MeC_6H_4CO_2^{\cdot}$ shows that $2\text{-}MeC_6H_4CO_2^{\cdot}$ almost completely converts to the benzyl radical, accompanied by no other reactions. Therefore it is reasonable to estimate the molar absorption coefficient of the benzoyloxyl radicals around 780 nm as nearly 1×10^3 M^{-1} cm^{-1} from that of the benzyl radicals (8.8×10^3 M^{-1} cm^{-1} for benzyl radicals at 316 nm in cyclohexane [21]).

4. Structural effects on the decarboxylation of aroyloxyl radicals

The aroyloxyl radicals, other than those undergoing intramolecular hydrogen-atom transfer, decay via decarboxylation in acetonitrile and carbon tetrachloride. According to the magnitude of the decarboxylation rate constants and the effect of acetonitrile as solvent on the decarboxylation, the aroyloxyl radicals can be classified into three groups as summarized in Table 2. These groups are described below in the sequence of III, II and I for convenience.

Group III consists of the benzoyloxyl radicals which bear substituents at the 2 and 6 positions, i.e. $2,6\text{-}Me_2C_6H_3CO_2^{\cdot}$, $2,6\text{-}Cl_2C_6H_3CO_2^{\cdot}$ and $2,4,6\text{-}Me_3C_6H_2CO_2^{\cdot}$. These radicals decarboxylate more rapidly than the others in both solvents. In particular, $2,6\text{-}Me_2C_6H_3CO_2^{\cdot}$ decarboxylates too rapidly for the rate constant to be determined exactly at ambient temperature. These three radicals decarboxylate more rapidly in carbon tetrachloride than in acetonitrile [12].

It is clear that steric congestion around the carboxyl radical centre by the two substituents at the 2 and 6 positions results in twisting of the carboxyl group from the aromatic ring plane and accelerates decarboxylation. As mentioned above, $2,6\text{-}Me_2C_6H_3CO_2^{\cdot}$ and $2,4,6\text{-}Me_3C_6H_2CO_2^{\cdot}$ undergo no intramolecular hydrogen-atom transfer from the adjacent methyl groups. The two methyl groups at the 2 and 6 positions prevent the radical centre from taking a conformation coplanar to an H–C bond of the methyl groups. The decarboxylation rate constant of $2,4,6\text{-}Me_3C_6H_2CO_2^{\cdot}$ is lower than that of $2,6\text{-}Me_2C_6H_3CO_2^{\cdot}$, but higher than that of $4\text{-}MeC_6H_4CO_2^{\cdot}$. This suggests that the introduction of a 4-methyl group contributes to the stabilization of $2,6\text{-}Me_2C_6H_3CO_2^{\cdot}$ as discussed below.

The much higher rate constants for decarboxylation of these radicals than the other benzoyloxyl radicals can be attributed to the decrease in the double bond character of the bond connecting the aromatic and carboxyl groups due to twisting and/or the increase in the O–C–O angle which accompanies the increase in the length of the above bond [12].

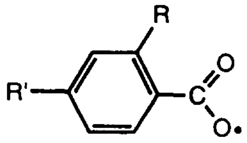
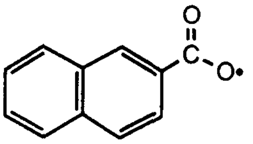
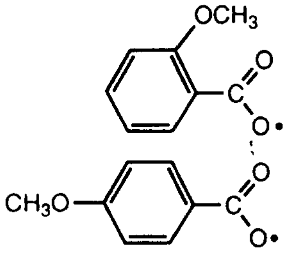
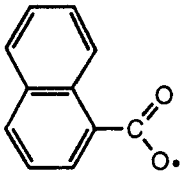
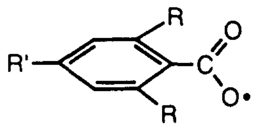
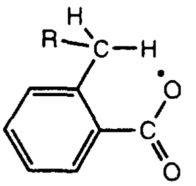
Group II contains $1\text{-}NpCO_2^{\cdot}$, $2\text{-}MeOC_6H_4CO_2^{\cdot}$ and $4\text{-}MeOC_6H_4CO_2^{\cdot}$. These radicals exhibit the slowest decay of the $ArCO_2^{\cdot}$ radicals examined. The rate constants in acetonitrile are much lower than those in carbon tetrachloride. In $2\text{-}MeOC_6H_4CO_2^{\cdot}$, the presence of the 2-methoxy group has no steric effect on the behaviour of the radical. Its stability can be attributed to intramolecular charge transfer from the methoxy group to the unsaturated moiety containing the carbonyl group as suggested for $4\text{-}MeOC_6H_4CO_2^{\cdot}$ [8,9] (Scheme 2).

In acetonitrile, $1\text{-}NpCO_2^{\cdot}$ decays via two-component kinetics of first and second order. A decrease in the peroxide concentration from 1×10^{-3} to 6.4×10^{-5} mol dm^{-3} leads to an increase in the apparent lifetime from 1.4 to 4.9 μs and gives clean first-order kinetics [10]. On the other hand, in carbon tetrachloride, the rate constant remains unchanged as a function of peroxide concentration. These results suggest that $1\text{-}NpCO_2^{\cdot}$ undergoes unimolecular decomposition which is too slow to compete with the bimolecular decay at high concentrations in acetonitrile. The second-order kinetics observed at high concentrations may be related to the formation of a bimolecular rearranged product as previously reported by Leffler and Zepp [22], as shown in Scheme 3. The remarkable stability of $1\text{-}NpCO_2^{\cdot}$ in acetonitrile can be attributed to the contribution of intramolecular charge transfer as depicted in Scheme 4 [10].

Group I is composed of $C_6H_5CO_2^{\cdot}$, $4\text{-}MeC_6H_4CO_2^{\cdot}$, $4\text{-}ClC_6H_4CO_2^{\cdot}$, $2\text{-}ClC_6H_4CO_2^{\cdot}$ and $2\text{-}NpCO_2^{\cdot}$. The decarboxylation rate constants for these radicals are not very different for the two solvents. This suggests that the contribution of intramolecular charge transfer to the stabilization of the radicals is less important in $2\text{-}NpCO_2^{\cdot}$ than in $1\text{-}NpCO_2^{\cdot}$ due to the smaller extent of conjugation at the 2 position than at the 1 position of the naphthalene nucleus. No contribution of intramolecular charge transfer is observed in $C_6H_5CO_2^{\cdot}$, $4\text{-}MeC_6H_4CO_2^{\cdot}$, $4\text{-}ClC_6H_4CO_2^{\cdot}$ and $2\text{-}ClC_6H_4CO_2^{\cdot}$.

Comparing group III with group I, the smaller rate constants of $2,6\text{-}Me_2C_6H_3CO_2^{\cdot}$, $2,6\text{-}Cl_2C_6H_3CO_2^{\cdot}$ and $2,4,6\text{-}Me_3C_6H_2CO_2^{\cdot}$ in acetonitrile than in carbon tetrachloride suggest a stabilization mechanism different from those described above. The substitution of a chlorine atom at the 2 position ($2\text{-}ClC_6H_4CO_2^{\cdot}$) instead of the 4 position ($4\text{-}ClC_6H_4CO_2^{\cdot}$) does not result in any change in the rate constants between the solvents. As discussed in Section 2, in

Table 2
Absorption maxima (λ_{max}) and rate constants (k) for decarboxylation of aroyloxyl radicals ($ArCO_2^{\bullet}$) at ambient temperature

$ArCO_2^{\bullet}$		λ_{max} (nm)	k (s^{-1})	
Group	Formula		In CH_3CN	In CCl_4
I	 R = R' = H; R = Cl, R' = H; R = H, R' = CH_3, Cl 	>800	10^6	10^6
II	 [a] 	>800	10^5	10^5–10^6
III	 R = CH_3, R' = H R = Cl, R' = H R = R' = CH_3	≈700	10^6–10^7	10^7–10^8
IV	 R = H, CH_3, Ph	>800	10^7 [b]	10^7 [b]

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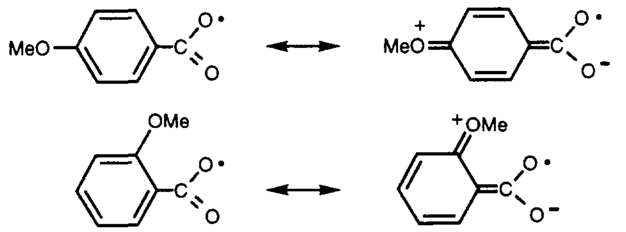
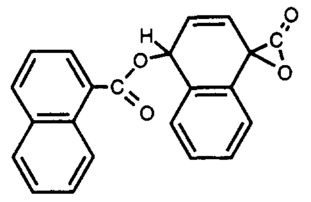
[a] The decay obeys second-order kinetics at high concentrations.

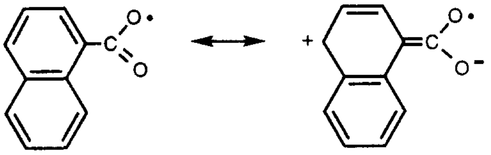
[b] Intramolecular hydrogen-atom transfer.



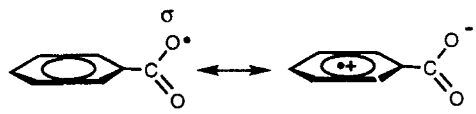
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

group III radicals, the aromatic π orbitals conjugate with the σ orbitals in the carboxyl plane. This conjugation may be accompanied by intramolecular charge transfer between the aromatic moiety and the σ orbitals particularly in acetonitrile as shown in Scheme 5. This may lower the spin density on the carboxyl oxygen atom leading to a reduction in the decarboxylation rate constants. A nearly tenfold decrease in the decarboxylation rate constant of $2,4,6\text{-}\mathrm{Me_3C_6H_2CO_2}^{\cdot}$ in acetonitrile from that in carbon tetrachloride shows that, even in the twisted conformation, the 4-methyl group can effectively act as an electron donor in acetonitrile.

In the case of $2\text{-}\mathrm{NpCO_2}^{\cdot}$, a lower ionization potential of the naphthalene nucleus than that of the benzene nucleus may lead to a type of intramolecular charge transfer similar to that between 1-naphthyl and carboxyl groups twisted with respect to each other.

In aroyloxyl radicals, no solvent effect on the absorption spectrum has generally been observed; however, the intramolecular charge transfer, if it occurs, is expected to contribute to stabilization to a higher extent in acetonitrile than in carbon tetrachloride. The failure to observe a solvent effect may be due to the difficulty in obtaining the absorption maximum within the wavelengths examined. Therefore it is worth noting that the absorption spectrum of $2,6\text{-}\mathrm{Cl_2C_6H_3CO_2}^{\cdot}$ is shifted slightly to longer wavelengths in acetonitrile than in carbon tetrachloride as shown in Fig. 6.

5. Conclusions

In general, the effect of the structure of aroyloxyl radicals on the absorption spectra and decarboxylation rate can be explained when the radicals are classified into four groups on the basis of the magnitude of the decarboxylation rate constants, the effect of polar solvents on decarboxylation and the reaction mode.

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