Electron Transfer in the Photochemistry of Substituted Benzoate and Naphthoate Esters[1]

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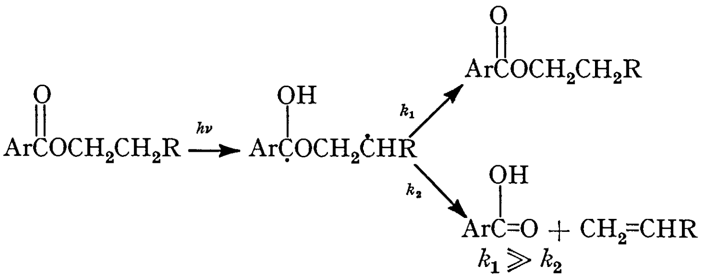
Substituted alkyl esters of aromatic carboxylic acids ($ArCO_2CH_2CH_2X$) undergo photochemical cleavage to give the carboxylic acid. If X is a dialkylamino- or methylthio-group, the reaction is relatively efficient (ϕ up to *ca.* 0.25), and this is attributed to the operation of an electron-transfer mechanism. Excited state lifetime measurements provide strong support for such a mechanism; in particular the singlet lifetime is at least six times shorter for esters containing the dialkylamino-group.

ONE of the most widely studied photochemical reactions of carbonyl compounds is the intramolecular photoelimination reaction known as the Norrish type 2 process, which results in the formation of a shorter-chain carbonyl compound and an alkene.[2] Ketones, aldehydes, carboxylic acids, esters, and other classes of compound undergo this reaction. The process is inefficient for alkyl esters of aromatic carboxylic acids ($\phi < 0.02$),[3,4] and the inefficiency is probably caused by effects in an intermediate biradical which make reformation of the ground state of the ester by reverse hydrogen-transfer to be greatly preferred over cleavage of the β-bond to give products [reaction (1)].



(1)

This occurs in spite of thermodynamic factors in the esters (higher excited state energy than for ketones, and greater bond strength for C=O in the acid formed from an ester than for C=C in the enol formed from a ketone) which should make both steps of the cleavage process more favourable than the corresponding steps for ketones. The different electronic nature of the lowest excited states, (π,π^*) for aromatic esters, but (n,π^*) for many aromatic ketones, must have a major influence on the relative rates for the first step, namely formation of the biradical, but the partitioning of the biradical is probably quite sensitive to conformational factors. These are held to be responsible for the low efficiency of the Norrish type 2 reaction of 2-alkylcyclohexanones,[5] and they may be important as a cause of the low efficiency of reaction for aromatic esters. Efficient cleavage requires that the orbitals containing the two unpaired electrons and the σ bond being broken be

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[1] Preliminary report, J. D. Coyle and D. H. Kingston, *Tetrahedron Letters*, 1975, 1021. (The absolute ϕ values are *ca.* 40% lower in the present paper because a solvent effect on the actinometer has been taken into account).

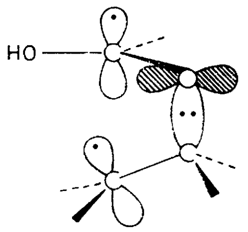
[2] J. A. Barltrop and J. D. Coyle, ' Excited States in Organic Chemistry,' Wiley, London, 1975, section 7.5.2; P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168 and references therein.

[3] J. A. Barltrop and J. D. Coyle, *J. Chem. Soc.* (*B*), 1971, 251.

[4] J. E. Gano, *Chem. Comm.*, 1971, 1491; J. G. Pacifici and J. A. Hyatt, *Mol. Photochem.*, 1971, **3**, 267, 271.

[5] J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop, and J. D. Coyle, *J. Amer. Chem. Soc.*, 1971, **93**, 7213.

parallel or nearly so [species (I)], but this can only be achieved in the biradical from an ester at the expense of the stabilisation afforded to one radical centre by a lone pair of electrons on the adjacent oxygen atom [shaded in (I)]. This conformation of the biradical may therefore be much more unfavourable than the corresponding one for ketones.



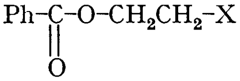
(I)

The biradical must be short lived, since optical activity at the site of hydrogen abstraction is lost only inefficiently by racemisation as a result of reversible hydrogen transfer.[4] Bond rotation in the biradical is apparently slower than back-transfer of the hydrogen atom. This is not unreasonable in view of the high rate constants estimated [6] for reactions of singlet 1,4-biradicals and the relatively high barriers to rotation suggested [7] for bond rotation in such species.

Because the aromatic esters have higher excited state energies than do aromatic ketones [*ca.* 5 kcal mol^{-1} (20 kJ mol^{-1}) difference in the lowest triplet states, and *ca.* 20 kcal mol^{-1} (85 kJ mol^{-1}) in the lowest singlet states],[3] it is possible that electron transfer occurs as a primary process in the excited state of the esters, and it was with this in mind that we initiated a study of benzoate and naphthoate esters substituted in the *O*-alkyl group.

RESULTS AND DISCUSSION

A series of benzoate esters (II) with substituents in the alkyl group were irradiated (254 nm) in cyclohexane



$$Ph{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}CH_2CH_2{-}X$$

(II)

solution, and the quantum yield for formation of benzoic acid was determined by converting the acid to its methyl ester using diazomethane and estimating the ester by g.l.c.

$$\begin{tikzcd} & & & \text{ground state} \\ \text{ground state} \arrow[r, "h\nu"] & \text{excited state} \arrow[r, "\phi\ ca.1"'] & \text{biradical} \arrow[ur, "k'_1"] \arrow[dr, "k'_2"'] & & (3) \\ & & & \text{products} \end{tikzcd}$$

$$\phi \simeq k_2'/(k_1' + k_2')$$

n-Propyl benzoate (II; X = Me) was used as a secondary actinometer,[3] and the relative quantum yields are reckoned to be accurate to ±10%, although the absolute values will also reflect errors in the actinometer quantum yield. The results are shown in Table 1.

Table 1

Photolysis of esters (II) in cyclohexane to give benzoic acid and alkenes

X	Me	Ph	OMe	OEt
ϕ	0.003 5	0.008_5	0.023	0.009 [a]
X	NMe_2	$\ulcorner CH_2\,CH_2 \urcorner$ $N{\cdot}CH_2{\cdot}CH_2{\cdot}O$	CH_2NMe_2	SMe
ϕ	0.15	0.1_5	0.018	0.08

[a] From ref. 8.

It is clear that those esters where X is a dialkylamino- or methylthio-group undergo much more efficient reaction than do the others. If there is no biradical intermediate in the reaction, the quantum yields must reflect the reactivity of the excited state towards hydrogen abstraction and cleavage (2).

$$\begin{tikzcd} & & \text{ground state} \\ \text{ground state} \arrow[r, "h\nu"] & \text{excited state} \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & & (2) \\ & & \text{products} \end{tikzcd}$$

$$\phi = k_2/(k_1 + k_2)$$

If there is a biradical intermediate, the quantum yield probably reflects the partitioning of the biradical [reaction (3)], since results for alkyl benzoates [3] suggest that excited state decay occurs largely by way of the biradical in these systems.

If scheme (2) operates, the substituent X is likely to affect the quantum yield mainly through its effect on the rate constant for hydrogen abstraction (k_2). If scheme (3) operates, the main effect is on the rate constant for reverse hydrogen transfer (k_1'). In either case, a lowering of the homolytic C–H bond strength at the site of reaction will cause an increase in quantum yield (k_2 increases or k_1' decreases). This seems to hold for the phenyl- and alkoxy-substituted esters (II; X = OMe, OEt, or Ph), whose reactions are 2—6 times as efficient as those of n-propyl benzoate. However, the dialkylamino- and methylthio-substituted esters undergo much (10—20 times) more efficient reaction. Since these latter groups should not have a greater effect on

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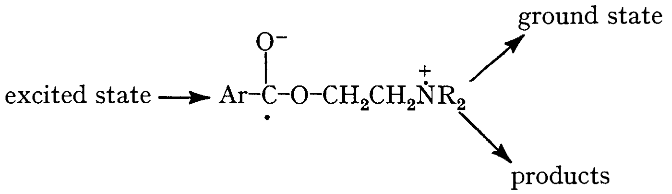
[6] C. P. Casey and R. A. Boggs, *J. Amer. Chem. Soc.*, 1972, **94**, 6457.

[7] L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, 1972, **94**, 4599.

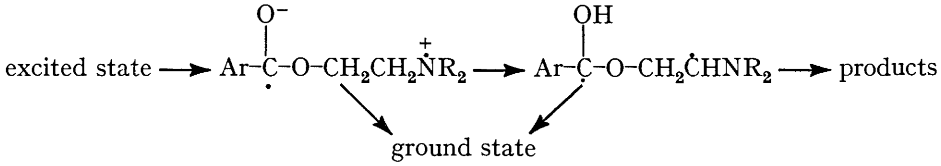
[8] R. Brainard and H. Morrison, *J. Amer. Chem. Soc.*, 1971, **93**, 2685.

the homolytic C–H bond strength than do phenyl or alkoxy-groups, this suggests that a different mechanism is operating. Electron transfer as a primary process is an attractive possibility, since it does occur in related sulphur or nitrogen compounds, such as ketones $PhCOCH_2CH_2CH_2NR_2$ for which excited state decay occurs *via* reversible electron transfer (although such transfer does not play a part in the Norrish type 2 reaction of the triplet state of the ketone).[9] Moreover, when an electron-transfer mechanism does operate, the efficiency is not greatly affected by the electronic nature (n,π^* or π,π^*) of the lowest excited state, whereas in hydrogen abstraction (π,π^*) states usually undergo reaction with a much lower efficiency.[10]

Electron transfer leads to a zwitterionic biradical, which can give products in competition with reverse electron transfer to produce ground state ester [reaction (4)], or which can undergo proton transfer to give a neutral biradical which then gives β-cleavage products [reaction (5)]. In the latter case, either intermediate may form ground state ester by a reverse transfer process.



$$\text{excited state} \longrightarrow Ar\overset{O^-}{\underset{\bullet}{C}}-O-CH_2CH_2\overset{+}{\dot{N}}R_2 \begin{cases} \nearrow \text{ground state} \\ \searrow \text{products} \end{cases} \qquad (4)$$



$$\text{excited state} \longrightarrow Ar\overset{O^-}{\underset{\bullet}{C}}-O-CH_2CH_2\overset{+}{\dot{N}}R_2 \longrightarrow Ar\overset{OH}{\underset{\bullet}{C}}-O-CH_2\dot{C}HNR_2 \longrightarrow \text{products} \qquad (5)$$

ground state

If a neutral biradical is formed, the system can give rise to a significantly higher quantum yield of reaction than that expected on the basis of direct hydrogen-atom transfer in the excited state only if the biradical is different in some way when formed from the zwitterion. This difference is unlikely to be one of spin multiplicity, since for unsubstituted alkyl benzoates both the singlet and triplet state reactions are inefficient.[3] The other likely difference is one of conformation, and this is reasonable if the second stage in the sequence zwitterion ⟶ biradical ⟶ products is fast compared with conformational changes, since the conformation in which the zwitterion is formed may well be very different from that in which a biradical would be formed from the excited state.

For most of the esters the type 2 process is the major reaction pathway, though chemical yields could not be determined accurately because the extent of reaction was limited to 10% or less in all cases. For 3-dimethylaminopropyl benzoate (II; $X = CH_2NMe_2$) the β-cleavage (type 2) reaction is not the major process and disappearance of ester is much more efficient (ϕ *ca.* 0.2). It is reasonable to suggest that electron transfer occurs in this ester, and that other reactions compete effectively with transfer of a proton from the unactivated second CH_2 group of the propyl unit.

Protonation of the nitrogen atom in the dimethylamino-substituted ester reduces the quantum yield by a factor >10 (Table 2), and this supports the view that an electron-transfer mechanism operates for the unprotonated ester, since there is no electron available for transfer from the ammonium nitrogen to the excited carbonyl group. The ' residual ' reaction in the protonated ester may occur by hydrogen-atom transfer or from the free dimethylaminoethyl benzoate in equilibrium with the salt.

Although acetonitrile is a very good solvent for electron transfer and cyclohexane is not, there is no large solvent effect on the quantum yield for reaction of (II; $X = NMe_2$). This may mean that the rate constant for the intramolecular electron-transfer step has no influence on the quantum yield for product formation. An interesting feature is that the quantum yield does not decrease with time in acetonitrile as significantly as it does in cyclohexane.

TABLE 2

Photolysis of esters (II) in acetonitrile

X	NMe_2	$\overset{+}{N}HMe_2Cl^-$
ϕ	0.13	0.011

A number of esters with different aromatic groups were employed to see how the efficiency of reaction is affected (Table 3). A ring substituent in the phenyl group, whether electron withdrawing or donating, does not have a very large effect on the quantum yield, which again may mean that the quantum yield is not

TABLE 3

Photolysis of $ArCO_2CH_2CH_2NMe_2$ (III) to give $ArCO_2H$ in cyclohexane

Ar	Ph	p-F-C_6H_4	p-MeO-C_6H_4	2-$C_{10}H_7$
ϕ	0.15	0.12	0.08_5	0.05

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[9] P. J. Wagner, A. E. Kemppainen, and T. Jellinek, *J. Amer. Chem. Soc.*, 1972, **94**, 7512.

[10] A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, 1969, **91**, 1857.

greatly influenced by the rate constant for the first step of the reaction. The quantum yield for the naphthoate ester, although only about one-third of the value for the benzoate, is relatively high; with alkyl carboxylates a change from benzoate to naphthoate causes a 50-fold reduction in quantum yield.[3] This lends support to a mechanism for the nitrogen-containing esters which is different from that involving hydrogen transfer in the primary step. Electron transfer is the most likely alternative, and in other systems where an electron-transfer mechanism operates (such as [11] photoreduction of 2-acetonaphthone by triethylamine) naphthyl compounds undergo reaction with an efficiency similar to that of phenyl compounds.

Quantum yields are not always a good guide to reactivity (rate constants), and in an attempt to determine the rate constants for the primary processes excited state quenchers were employed, penta-1,3-diene as a triplet state quencher and biacetyl as a singlet and triplet state quencher. Neither quencher has a significant effect on the reaction of dimethylaminoethyl benzoate (Table 4).

TABLE 4

Photolysis of (II; X = NMe_2) in the presence of quenchers

Quencher	None	Pentadiene (0.1M)	Biacetyl (0.1M)
ϕ	0.15	0.16	0.14

This means that the excited state responsible for reaction must be very short-lived ($\tau \leqslant 5 \times 10^{-10}$ s, assuming that 20% quenching would have been detected and that the rate constant for quenching is 5×10^9 l mol^{-1} s^{-1}), and it is in keeping with the measured singlet lifetime (see Table 5).

TABLE 5

Excited state lifetimes

	τ_p/s [a]	τ_T/μs [b]	τ_S/ns	ϕ_f [d]
$PhCO_2Me$	2.4_5	25	1.0	0.008 6
(II; X = Me)	2.6	20	2.7	0.080
(II; X = Ph)	2.5	14	1.2	0.030
(II; X = OMe)	2.4_5	$\leqslant 10$	1.1_5	0.028
(II; X = NMe_2)	2.2	<5	0.12	0.004
(II; X = CH_2NMe_2)	2.2_5	<5	0.35	0.014
(II; X = $\overset{+}{N}HMe_2Cl^-$)		<5	0.40	0.013
(III; Ar = *p*-$MeOC_6H_4$)	2.2	<5	0.14	0.002 5
2-$C_{10}H_7CO_2Me$	2.3	66 [c]	60	0.30
(III; Ar = 2-$C_{10}H_7$)	2.5	27 [c]	9.2	0.047

[a] In 2-methylpentane glass at 77 K. [b] In paraffin (η 167 cp). [c] In cyclohexane. [d] Relative to naphthalene, biphenyl, and aminonaphthalene standards.

An alternative source of rate constant data involves measurement of excited state lifetimes, and these measurements were carried out to determine the triplet lifetime at 290 K, the triplet (phosphorescence) lifetime at 77 K, and the singlet (fluorescence) lifetime at 290 K, all in carefully degassed solution. The results are given in Table 5, together with the quantum yields for fluorescence. Typical triplet–triplet absorption spectra, for methyl benzoate and for dimethylaminoethyl benzoate, are shown in Figure 1.

Two important features emerge from these results. First, the introduction of a phenyl or methoxy-substituent in the alkyl chain lowers the lifetimes, those at 290 K by a factor of *ca.* 2. This is in accord with a hydrogen-transfer mechanism through a biradical intermediate [reaction (3)]. The alternative mechanism without a biradical [reaction (2)] can less easily accommodate these results, since the major pathway followed by the excited state is direct (and rapid) decay to ground state, which should not be greatly affected by a remote substituent.

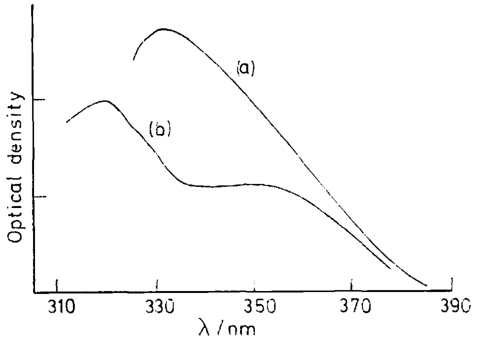

FIGURE 1 Triplet–triplet absorption spectra of (a) $PhCO_2Me$ and (b) $PhCO_2CH_2CH_2NMe_2$ in cyclohexane (10 μs delay)

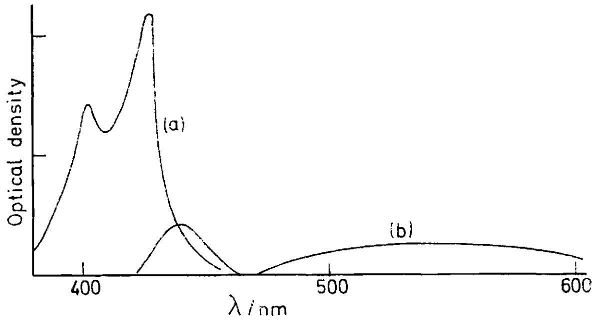

FIGURE 2 Absorption spectra of transients from 2-$C_{10}H_7CO_2Me$ in cyclohexane: (a) triplet (35 μs delay) and (b) species derived from triplet (120 μs delay)

Secondly, the esters containing the dialkylamino-group show substantially lower singlet and triplet lifetimes at 290 K, even when the group is separated from the ester group by three rather than two CH_2 units. This strongly supports the suggested electron transfer as the primary step, although it does not distinguish between mechanisms (4) and (5); excited state lifetime measurements can give direct information only about the primary steps. If the lifetime is governed largely by the rate constant for electron transfer, then this rate constant can be estimated to be *ca.* 8×10^9 s^{-1} for (II; X = NMe_2).

For the naphthoate esters, the singlet lifetime [12] and the quantum yield for fluorescence are both reduced by

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[11] S. G. Cohen, G. A. Davis, and W. D. K. Clark, *J. Amer. Chem. Soc.*, 1972, **94**, 869.

[12] M. Kitamura and H. Baba, *Bull. Chem. Soc. Japan*, 1975, **48**, 1191 have recently quoted τ_S = 38.4 ns, ϕ_f = 0.32 for methyl 2-naphthoate at 77 K.

a factor of 6 on changing from methyl to dimethylaminoethyl 2-naphthoate. This is in accord with the occurrence of rapid electron transfer in the singlet state of the nitrogen-containing ester. The triplet lifetime at 290 K is also shorter for the nitrogen-containing ester, but in both cases a second species is detected which is not present immediately after the flash, but which is formed from the triplet state and then undergoes first-order decay. Its spectrum is very different from that of the triplet (Figure 2; the triplet–triplet absorption spectrum is similar to that of naphthalene), and its lifetime is different (50 μs for the intermediate from methyl 2-naphthoate, 90 μs for the intermediate from dimethylaminoethyl 2-naphthoate), but at present it is not possible to assign a structure to this intermediate.

EXPERIMENTAL

The esters were prepared from the acid or acid chloride by standard procedures and purified by recrystallisation or distillation. Irradiations were carried out in quartz reaction tubes in a Rayonet RPR-208 photochemical reactor (Southern New England Ultraviolet Co.) with merry-go-round MGR-100 attachment and RUL 2537 Å lamps. The solutions were generally *ca.* 0.1M in ester and contained straight chain alkane (*ca.* 0.004M) as internal standard for g.l.c. Samples were taken at intervals, and reaction was generally carried to <10% conversion, often <2%; results were extrapolated to zero conversion. The acid produced was converted into its methyl ester with excess of diazomethane, and g.l.c. analysis was carried out on a column made up as 10% Carbowax 20M on Kieselguhr.

Conventional and picosecond flash photolysis and single-photon counting was carried out using equipment at the Royal Institution.[13] The error in the singlet lifetimes is around ±0.05 ns for $\tau_S > 2.5$ ns, ±0.15 ns for τ_S *ca.* 1.2 ns, and ±50% for $\tau_S < 0.5$ ns. Fluorescence and phosphorescence measurements were made using a Perkin-Elmer MPF 4 instrument with Hitachi S10 photomultiplier. Spectra were fully corrected and were recorded under conditions where they were independent of concentration. All solutions were thoroughly degassed by several freeze–pump–thaw cycles, and lifetimes quoted are the average of 2—4 separate readings.

We thank the S.R.C. for a grant to purchase the Rayonet photochemical reactor. We are grateful to Dr. A. Harriman of the Royal Institution for assistance in the luminescence and lifetime measurements, and to the Royal Institution for permission to use its specialist equipment.

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[13] G. Porter and M. A. West, in 'Techniques in Organic Chemistry,' eds. A. Weissberger and G. Hammes, Wiley, New York, 1973, vol. 6.