Photochemical Behaviour of Acridine in the Presence of Carboxylic Acids

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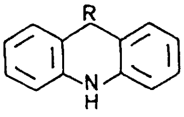
Summary The interaction of photoexcited acridine with carboxylic acids is shown to yield radical pairs *via* simultaneous or consecutive proton and electron transfer from the carboxyl groups to the acridine.

The photochemistry of acridine and related systems has been extensively investigated and attention has been drawn to the similarity between the C=N chromophore and the C=O chromophore in their ability to abstract hydrogen atoms from alkyl residues.[1] Abstraction of hydrogen atoms from other residues has only rarely been observed.[2]

RCO_2H

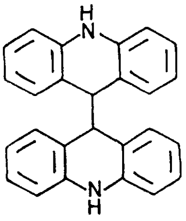
(2)



(3)

R–R

(4)



(5)

Noyori *et al.*[3] found that nitrogen heterocyclic compounds may undergo light induced reductive alkylation by some carboxylic acids while being inert towards others. These differences were however not understood. This communication describes evidence for the formation of a radical pair on interaction of photoexcited acridine (**1**) with phenylacetic acids *via* simultaneous or consecutive proton and electron transfer from the acid to the acridine.

Table. Photochemical reactions of acridine with carboxylic acids

Carboxylic acid (**2**)	Quantum yield[a,b]	Chemical yield[c]/% (**3**) (m.p.)	(**4**)	(**5**)
(**a**); R=*p*-$MeOC_6H_4CH_2$-	0.27^d (0.33^e; 12^f 0.065^g)	53(193—196 °C)	12	
(**b**); R=*p*-$MeC_6H_4CH_2$-	0.24^d	48(193—195 °C)	10	10
(**c**); R=$PhCH_2$-	0.23^d	72^h		10^h
(**d**); R=*m*-$MeOC_6H_4CH_2$-	0.22^d	50(142—145 °C)	10	
(**e**); R=*p*-$FC_6H_4CH_2$-	0.20^d	62(180—182 °C)		10
(**f**); R=$PhOCH_2$-	0.29^d	82(164—166 °C)		
(**g**); R=$PhSCH_2$-	0.25^d	45(118—120 °C)		12
(**h**); R=Et-	0.14^d	31^h		17^h
(**i**); R=$MeOCH_2$-	0.23^d	71(110—112 °C)		
(**j**); R=CF_3	$<0.02^{d,i}$			

[a] Concentration of acridine 10^{-1} M; concentration of carboxylic acid, 10^{-1} M. [b] Excitation wavelength 366 nm. [c] Chemical yield of isolated material relative to consumed starting material. [d] 4% (volume) t-Butyl alcohol–benzene solution. [e] Benzene solution. [f] Acetonitrile solution. [g] t-Butyl alcohol solution. [h] See ref. 3. [i] Concentration of acridine 2.5×10^{-2} M; concentration of acid 10^{-1}M.

We found that solutions of acridine (**1**) and carboxylic acids (**2a**)—(**2i**) exhibit u.v. absorption spectra characteristic of mixtures of free acridine and acridine associated with the respective acids *via* hydrogen-bonding,[4] while solutions of acridine (**1**) and trifluoroacetic acid (**2j**) exhibit u.v. spectra indicating mixtures of free acridine (**1**) and protonated acridine.[4] The addition of 0·1 M *p*-methoxyphenylacetic acid (**2a**) to a solution of acridine (**1**) in 4%(volume) t-butanol–benzene did not effect the fluorescence spectrum of (**1**) significantly, but addition of 0·1 M trifluoroacetic acid (**2j**) resulted in a dramatic enhancement and bathochromic shift of the fluorescence of (**1**), characteristic of the acridinium ion.[5]

Irradiation of a benzene solution of acridine (**1**) (0·1 M) and *p*-methoxyphenylacetic acid (**2a**) (0·1 M) with a medium pressure mercury lamp (Pyrex filter) at room temperature resulted in rapid consumption of both components and gave the adduct (**3a**) and 1,2-di-*p*-methoxyphenylethane (**4a**) which were isolated by chromatography on silica gel, [(**3a**), m.p. 193—196 °C; u.v. λ_{max} (EtOH) 287 nm (ϵ 17,550); n.m.r. (C_6D_6) δ 2·80 (2H, d, *J* 7 Hz, $ArCH_2$), 3·245 (3H, s, CH_3O-), 4·02 (1H, t, *J* 7 Hz, Acr*CH*Acr), 5·22 (1H, m, N*H*) and 6·2—7·8 (12H, m, Acr*H* and Ar*H*); *m/e* 301]. Acridine (**1**) reacted under analogous conditions with the carboxylic acids (**2b**)—(**2i**) to give the addition products (**3b**)—(**3i**) in good to excellent yields together with small amounts of the dimer (**5**) and bibenzyl derivatives (**4**) (Table). The structures of all new compounds were established by their spectroscopic and analytical properties. *p*-Methoxyphenylacetic acid ethyl ester failed to react with photoexcited acridine under analogous reaction conditions, [$\phi < 0.05$] as did trifluoroacetic acid (**2j**).

The quantum yields for the consumption of acridine in the presence of the acids (**2a**)–(**2e**) were dependent on the acid and were higher in benzene than in t-butanol or acetonitrile solution (Table). For the phenylacetic acids (**2a**)—(**2e**) the quantum yields correlate approximately with the σ constants introduced by Dippy[6] giving a negative ρ value.

CIDNP studies[7] provided direct evidence for the intermediacy of a radical pair in the photochemical reductive alkylation of acridine by carboxylic acids. Thus a multiplet E/A effect for the triplet of the methine proton (Acr*CH*Acr) and the doublet of the methylene protons ($ArCH_2$) in the addition product (**3**), and a net E effect for the aromatic proton at position 9 (δ 8·08) of the regenerated acridine (**1**) were observed during irradiation of a solution of acridine (**1**) and the acid (**2a**) in the cavity of the n.m.r. spectrometer. Assuming that the singlet state† is the precursor of the radical pair, the sign of the multiplet E/A effect, $\Gamma_m = \mu.\epsilon.a_i.a_j.J_{ij}.\sigma_{ij} = - + - - + - +^8 = +$ suggests

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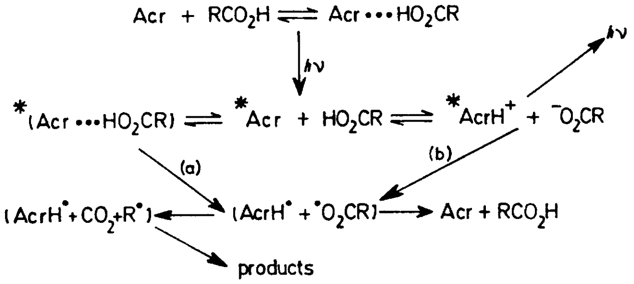
† The negligible effect of air on the efficiency of the photoreaction suggests the involvement of the singlet state.

that the adduct (**3**) is formed by recombination within the original cage, while the polarization of the proton at position 9 of the acridine (**1**) indicates the occurence of a reversible hydrogen transfer from the acid to the heterocyclic system. The level of net polarization of (**1**) is significantly higher than that of (**2**) indicating, as one of the referees pointed out, that (**1**) and (**3**) might arise from different radical pairs. The precursor of (**1**) exhibiting a larger value of Δg could thus be $(ArCH_2CO_2\cdot \ldots \cdot HAcr)$[8], the precursor of (**3**) $(ArCH_2\cdot \ldots \cdot HAcr)$[8].



Scheme

These findings suggest that irradiation of an equilibrium mixture of acridine and acridine associated with the respective carboxylic acid *via* hydrogen bonding results in the formation of a rapidly equilibrating mixture of electronically excited free acridine, acridine hydrogen-bonded to the respective acid, and protonated acridine. This system may either deactivate *via* radiative processes or form radical pairs *via* hydrogen transfer [path (a)] or *via* consecutive proton and electron transfer from the carboxy group to the acridine [path (b)]. The radical pairs may regenerate acridine, combine to give addition products (**3**), or escape the solvent cage to give reduction products (**4**) and (**5**).

Abstraction of hydrogen from a hydrogen-bonding carboxy group might become favoured over abstraction of a hydrogen from a benzyl residue, particularly when the former occurs with subsequent loss of carbon dioxide which results in the formation of a stable radical pair. The observed Hammett correlation for the quantum yields, the higher efficiency of the photoreaction in benzene than in acetonitrile and the CIDNP data are compatible with this Scheme. Weak acids and non-polar solvents favour those pathways which lead to the formation of the radical pair; thus hydrogen transfer from the carboxy group to the photoexcited acridine will occur in preference to proton transfer.[9] Similarly electron transfer from the carboxylate anion to the acridinium ion will compete favourably with radiative deactivation of the acridinium ion.[5] The occurence of chemical transformation subsequent to light induced hydrogen transfer from other than alkyl residues might be an ubiquitous phenomenon whose scope and limitations are under present investigation.

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