

N-DEALKYLATION OF ELECTRONICALLY EXCITED COUMARINS BY NITROBENZENES[†]

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Summary

When excited (monochromatically or with $\lambda \geq 280$ nm) in benzene solution in the presence of nitroaromatic acceptors, several 7-dialkylaminocoumarins undergo moderately efficient mono-*N*-dealkylation to form 7-alkylaminocoumarins, accompanied by the reduction of the nitro function in the acceptor. For 7-(*N,N*-diethylamino)-4-methylcoumarin (1a) a linear plot of ϕ_p^{-1} versus the reciprocal of the concentration of the starting material suggests that two molecules of 1a are involved in the dealkylation of irradiated 1a by ground state 3-chloronitrobenzene. When the concentration of 1a is kept constant but that of the acceptor is varied, ϕ_p goes through a maximum at intermediate concentrations. Furthermore, ϕ_p is found to be larger for weaker acceptors (more negative reduction potential) than for stronger acceptors (less negative reduction potential). The rigid dye Coumarin 102 does not show any analogous decomposition. All results are interpreted in terms of the interference of the nitroaromatic with the self-quenching mechanism of coumarin *N*-dealkylation put forward recently by Jones and coworkers.

1. Introduction

N,N-Dimethylaniline may be oxidatively dealkylated to *N*-methylaniline, formanilide and even aniline by electronically excited benzophenone [1, 2], rose bengal [1] or methylene blue [1]. Similarly photoexcited 3-chloronitrobenzene (2d; see Fig. 1 for definition of structures) was shown to transform *N,N*-dimethylaniline into *N*-methylaniline and *N*-methylformanilide [3], and the dealkylation of both secondary and tertiary aliphatic amines by photoexcited nitrobenzenes has been studied in some detail [4].

Initial electron transfer from the ground state amine to the electronically excited nitroaromatics has been proposed for the aforementioned

[†]Taken in part from the doctoral thesis of Jörg Heufer, Universität Duisburg, 1984. Dedicated to Professor D. Schulte-Frohlinde on the occasion of his 60th birthday.

interactions, ultimately resulting in dealkylation [4, 5]. Likewise the reverse process, namely electron transfer from an excited tertiary alkylarylamine to a ground state acceptor, should also serve as an initiating step in amine dealkylation. Singlet ion pair formation has been demonstrated for the interaction of electronically excited *N,N*-dimethylanilines with 4-substituted acetophenones [6] (accompanied by energy transfer from the amine to the ketone and subsequent formation of triplet radical ion pairs, the latter being the product of the reaction of triplet excited ketones with *N,N*-dimethylanilines).

When being selectively excited in benzene solution in the presence of various nitrobenzenes, Michler's ketone and 4-nitro-*N,N*-dimethylaniline undergo a moderately efficient mono-*N*-dealkylation concomitant with the reduction of the acceptor [7]. 7-Dialkylaminocoumarins (1a - 1f) may also be regarded as *N,N*-dialkylanilines which absorb long wavelength UV light.

In this study, we report our results on the mono-*N*-dealkylation of excited coumarins 1a - 1f to 3a - 3f in benzene solution in the presence of nitrobenzenes acting as electron acceptors. This work should be seen in the context of recent research on the "self-dealkylation" of 7-dialkylaminocoumarins in solution [8 - 11] and investigations on electron donor-acceptor quenching and photoinduced electron transfer [12] as well as singlet energy transfer [13] of such dyes.

2. Experimental details

Laser-grade commercially available samples of 7-(*N,N*-diethylamino)-4-methylcoumarin (1a), 7-(*N,N*-dimethylamino)-4-methylcoumarin (1b), 7-(*N,N*-dimethylamino)-4-trifluoromethylcoumarin (1c), (7-*N,N*-diethylamino)-3-(2-benzimidazolyl)coumarin (1d), 7-(*N,N*-diethylamino)-3-(1-methylbenzimidazol-2-yl)coumarin (1e), 7-(*N,N*-diethylamino)-3-(2-benzthiazolyl)coumarin (1f) and 9-methyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*i,j*]quinolizin-11-one (4) were checked for impurities by means of thin-layer chromatography using chloroform-methanol (20:1 by volume) and toluene-ethyl acetate (10:1 by volume) and in most cases were used as received.

2.1. Dealkylations on a preparative scale

Nitrogen-purged benzene solutions (500 ml) containing both coumarin and 3-chloronitrobenzene (2d; see Table 1 for quantities used) were irradiated in a recycling reactor fitted with a 150 W high pressure mercury burner surrounded by a water-cooled Duran ($\lambda \geq 280$ nm) immersion well. After irradiation, the solutions were evaporated to dryness, and any excess 2d was removed by vacuum sublimation.

The residue was subjected to preparative layer chromatography on 48 cm \times 20 cm plates covered with air-dry silica gel (thickness, 1 mm) using chloroform-methanol (20:1 by volume) for irradiated samples of 1a, 1d - 1f

TABLE 1

Irradiation ($\lambda \geq 280$ nm) of coumarins 1a - 1f in benzene solution in the presence of 3-chloronitrobenzene (2d)

Starting material	Weight used (mmol)	Weight of 2d used (mmol)	Irradiation time (h)	Conversion ^a of 1 (%)	Product	Yield ^a (%)	Melting point (°C)
1a	4.0	12.0	4.5	24	3a	91	151 - 152
1b	0.6	3.0	7.0	65	3b	99	170 - 171
1c	0.6	3.0	7.0	75	3c	71	185
1d	1.0	6.0	8.0	13	3d	76	243 - 245 ^b
1e	1.0	6.0	8.0	16	3e	74	320 - 321
1f	1.0	6.0	8.0	38	3f	78	257 - 258

^aBased on starting material not recovered.

^bDecomposes.

and 4 and using toluene-ethyl acetate (3:1 by volume) in the cases of 1b and 1c. The starting material 1 and the product 3 were eluted with acetone-methanol from their respective zones and were crystallized from benzene-cyclohexane (5:1 by volume). All *N*-monoalkylcoumarins isolated gave satisfactory elemental analyses and were characterized by their IR, proton nuclear magnetic resonance and mass spectra. 3-Chloroacetanilide may be isolated upon treatment of the residue with acetic anhydride, followed by chromatographic separation. No attempt was made in this study to account for all reduction products of the nitroaromatic acceptors.

2.2. Determination of quantum yields

For the determination of the quantum yields of starting material decomposition and product formation, solutions of 1 and 2 (both 0.0128 M) in benzene were irradiated under argon using the 366 nm emission of a super pressure mercury burner (Osram HBO 200 W) isolated by means of a Bausch & Lomb high intensity monochromator and directed into the sample cell through a quartz condenser and a beam splitter. 9% of the light emitted from the monochromator was used for standard ferrioxalate actinometry [14]. The sample cell and the concentration were adjusted so that all the light entering the cell was absorbed, and this was checked by using another actinometer cell behind the sample cell. After irradiation, the samples were worked up as described above and the residue was subjected to layer chromatography. The starting material 1 and the product 3 were quantitatively eluted from their separated zones and were determined photometrically.

3. Results

Coumarins 1a - 1f did not show any conversion or degradation when irradiated with the Duran-filtered light ($\lambda \geq 280$ nm) of a 150 W high

pressure mercury burner in benzene solution for 10 h. Upon irradiation in the presence of 2d under otherwise identical conditions, however, significant amounts of the mono-*N*-dealkylated products 3a - 3f are formed (see Table 1). Under the conditions used, practically all of the incident light is absorbed by coumarins 1a - 1f and only a small fraction (if any) of the 313 nm emission can be absorbed by the nitroaromatic. In the quantitative experiments reported below, however, monochromatic light was used to eliminate this complication.

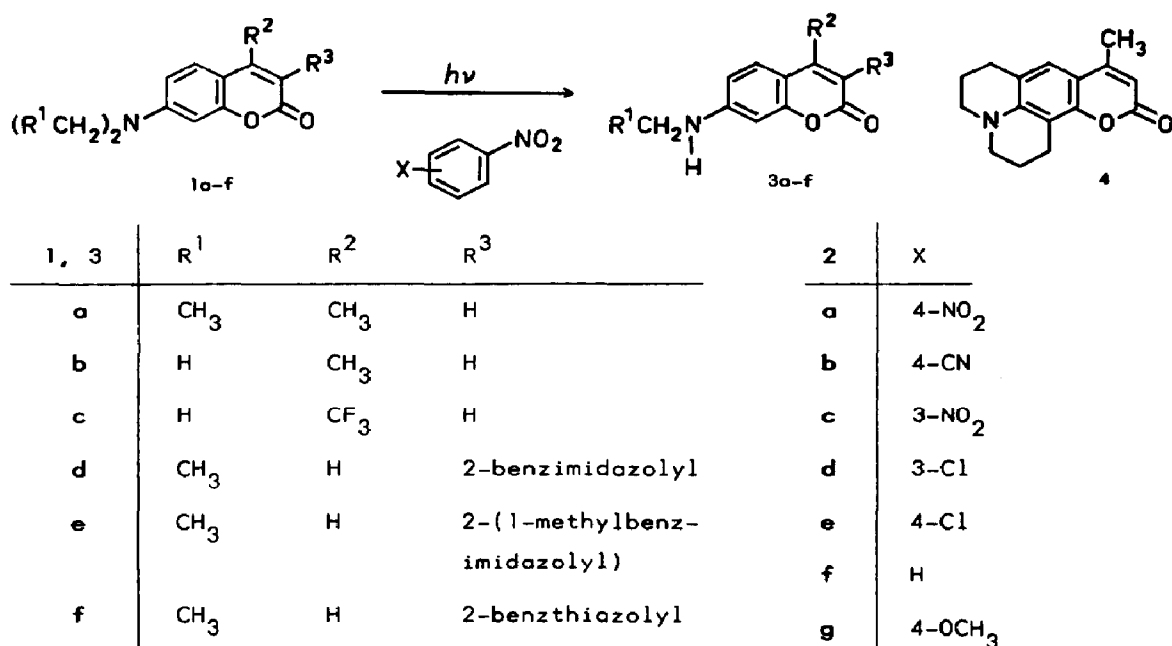


Fig. 1. Irradiation of 7-alkylaminocoumarins.

The choice of solvent is crucial. In a standard experiment, using 4 mmol 1a and 12 mmol 2d in 500 ml benzene, 40% conversion of 1a was reached within 6 h, but only 4% - 5% conversion could be achieved within a period of 14 h irradiation using acetonitrile as the solvent. No conversion at all was observed even after 20 h irradiation of a solution of 1a in methanol containing 2d.

The values of the integral quantum yields ϕ_d and ϕ_p for starting material conversion and appearance of dealkylated product respectively reveal that acceptors with a low negative reduction potential are less effective than acceptors with a more negative reduction potential (Tables 2 and 3).

For coumarin 1a, a complex dependence of dealkylation efficiency (as given by ϕ_p) on acceptor concentration has been observed (see Fig. 2).

As demonstrated for three different acceptors, ϕ_p shows a sharp rise at $[A] > 3 \times 10^{-3}$ M, peaks at around 10^{-2} M and then steadily decreases until it reaches a stable level at $[A] \geq 5 \times 10^{-2}$ M. Both peak value and final level

TABLE 2

Quantum yield ϕ_d for consumption of photoexcited ($\lambda = 366$ nm) 7-diethylamino-4-methylcoumarin (**1a**) and quantum yield ϕ_p for formation of the *N*-dealkylated product **3a** in benzene solution in the presence of nitrobenzenes **2a** - **2g** at room temperature

	<i>Acceptor</i>						
	<i>2a</i>	<i>2b</i>	<i>2c</i>	<i>2d</i>	<i>2e</i>	<i>2f</i>	<i>2g</i>
$E_{1/2}^a$ (V vs. SCE)	-0.700	-0.875	-0.910	-0.945	-0.965	-1.15	-1.25
ϕ_d (± 0.003)	0.005	0.012	0.015	0.045	0.028	0.050	0.057
ϕ_p (± 0.003)	—	0.011	0.012	0.044	0.03	0.049	0.055

SCE, standard calomel electrode.

^aIn acetonitrile solution; taken from ref. 15.

TABLE 3

Quantum yield ϕ_d for starting material consumption and quantum yield ϕ_p for product formation in the *N*-dealkylation of photoexcited coumarins **1b** - **1f** by various nitrobenzene acceptors in benzene solution at room temperature

<i>Coumarin</i>	<i>Excitation</i> (nm)	<i>Acceptor</i>	ϕ_d (± 0.004)	ϕ_p (± 0.004)
1b	366	2a	a	a
	366	2d	0.07	0.07
	366	2g	0.086	0.085
1c	366	2a	0.03	0.025
	366	2g	0.13	0.13
1d	410	2a	0.049	0.048
	400	2d	0.037	0.037
	410	2g	0.072	0.073
1e	400	2d	0.037	0.037
1f	410	2d	0.043	0.047

^aBelow detection limit.

are highest for the weakest acceptor tested and both are smallest for the best acceptor used in this study.

A linear plot of ϕ_p^{-1} versus $[1a]^{-1}$ (Fig. 3) suggests that the interaction of two molecules of the starting material **1a** is the rate determining step of the dealkylation reaction.

The tetracyclic dye **4** (Coumarin 102) does not undergo ring opening analogous to dealkylation when treated in the same way as coumarins **1a** - **1f** and is recovered unchanged. This finding parallels the inertness of *N*-phenylpyrrolidine, *N*-phenylpiperidine and *N*-phenylmorpholine as well as julolidine towards photoexcited nitrobenzenes [7], whereas "open" *N,N*-dialkyl-

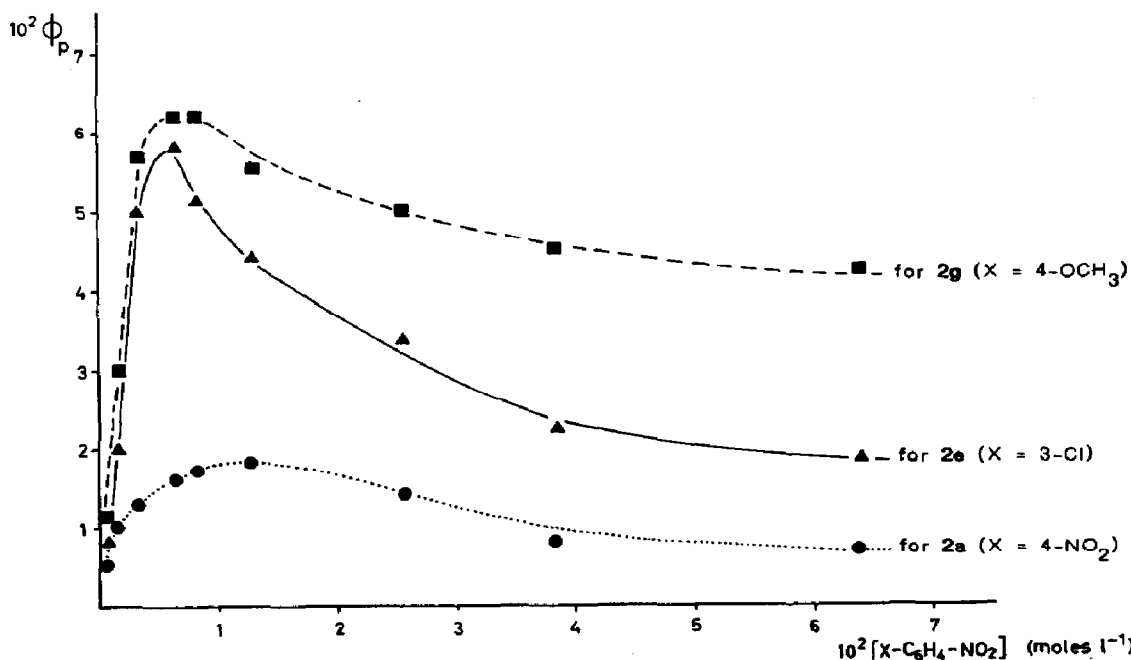


Fig. 2. Plot of product formation quantum yield ϕ_P for *N*-de-ethylation of 1a (1.28×10^{-2} M) vs. acceptor concentration [A] for acceptors 2a (●; X \equiv 4-NO₂), 2e (▲; X \equiv 3-Cl) and 2g (■; X \equiv 4-OCH₃).

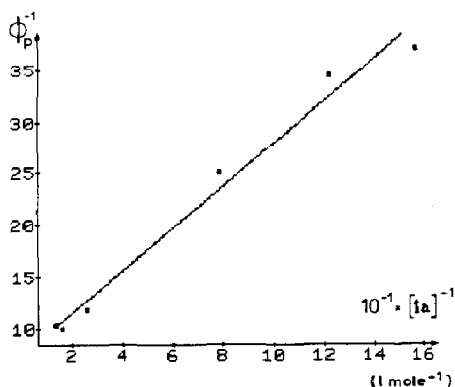


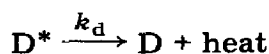
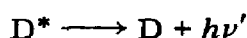
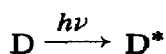
Fig. 3. Plot of ϕ_P^{-1} for formation of 3a vs. $[1a]^{-1}$ from the reaction of excited 1a with 3-chloronitrobenzene.

anilines tend to be dealkylated by such excited acceptors [3, 7]. Jones *et al.* [10] also noted that in deaerated solutions a "rigid" coumarin structure similar to that of 4 decomposes at a much slower rate than coumarins such as 1a - 1f.

4. Discussion

Recently, Jones and coworkers [10, 11] suggested a self-quenching mechanism for the relatively inefficient photodegradation (a limiting value

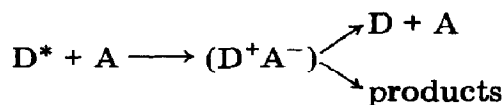
of 3×10^{-4} was given for the quantum yield of product formation) of several 7-dialkylaminocoumarin dyes (D in reactions below), including 1a, upon irradiation in acetonitrile solution.



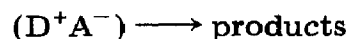
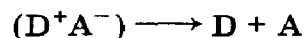
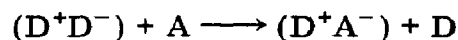
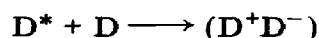
A calculation (from electroanalytical data) of the free energy change ΔG associated with electron transfer within a singlet excimer (0.5 kcal mol⁻¹) led to the conclusion [11] that, in acetonitrile solvent, electron transfer followed by proton transfer is an unimportant process in dye destruction.

The presence of nitroaromatic acceptors A, together with the use of benzene as a solvent, however, markedly increases the dealkylation efficiency (see Tables 2 and 3) compared with that observed in the self-quenching of coumarins in acetonitrile [11]. It is therefore suggested that A may interact with the self-quenching system [10, 11] in the following ways.

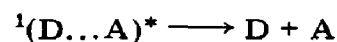
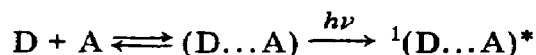
(1) Quenching of D* and/or product formation from an exciplex or an intimate ion pair:

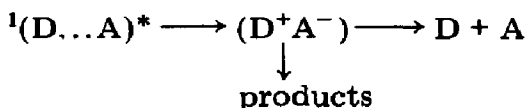


(2) Electron capture by A from an excimer or ion pair (D⁺D⁻) and liberation of D:



(3) Ground state complexation of D, thus allowing for excitation of the charge transfer (CT) complex:





Since a plot of ϕ_p^{-1} versus $[\text{D}]^{-1}$ is linear, the sequence of events listed in (2) seems to override that in (1) at $10^{-3} \text{ M} \leq [\text{A}] \leq 10^{-2} \text{ M}$ (Fig. 2). The formation of weak ground state complexes and thus the sequence of events listed in (3) seems to become important at $[\text{A}] > 10^{-2} \text{ M}$, although distinct shifts of the onset of absorption of solutions containing both 1a and acceptor towards longer wavelengths could be detected with certainty only for 2-nitronaphthalene (concentration, $10^{-3} - 10^{-2} \text{ M}$) as the acceptor. If ground state complexation is also effective with the nitrobenzene acceptors used in this study, it would in turn decrease the probability for the steps listed in sequence (2). For further interpretation of the fall-off in efficiency with increasing $[\text{A}]$ it is assumed that the excited CT complexes ${}^1(\text{D}\dots\text{A})^*$ predominantly tend to return to the ground state instead of going on to give products via an ion pair (D^+A^-). In accord with this view is the finding that acceptors with a low negative reduction potential (and which are thus capable of forming stronger ground state complexes) are less potent in effecting dealkylation (via sequence (2)) than acceptors with more negative reduction potentials. Finally, a quasi-stationary situation is reached at $[\text{A}] \geq 5 \times 10^{-2} \text{ M}$.

The high concentrations of ground state reactants necessary to observe weighable amounts of products, together with the use of benzene as the solvent, causes some difficulty in connecting the findings reported here with the results of photophysical investigations (usually carried out in dilute acetonitrile solutions) [12] or with electrochemical data [12] (also obtained for acetonitrile solutions).

Benzene seems to be a solvent which is especially suitable for the promotion of reactions within the ion pairs and for preventing the separation of the pairs before a sequence of steps (resulting ultimately in dealkylation, as outlined for compound 1a in Fig. 4) has taken place.

The scheme in Fig. 4, which involves the formation of nitrosoaromatics and aldehydes, is essentially a suggestion based on our findings in the *N*-dealkylations of tertiary amines by electronically excited nitroaromatics. Thus, 4-nitroso-*N,N*-dimethylaniline is produced in the base-promoted "self-dealkylation" of 4-nitro-*N,N*-dimethylaniline under irradiation [16]. It is very likely that other nitrosobenzenes are formed but are efficiently photo-reduced further in the photodegradation of tertiary aliphatic amines by photoexcited alkyl nitrobenzenes, and may be regenerated in the reaction mixture by air oxidation [4]. Benzaldehyde is formed in over 77% yield (and is ultimately characterized as benzoic acid by air oxidation) in the *N*-debenzylation of *N,N*-dibenzylaniline by excited 2a [7] and it has recently been claimed that glycolic aldehyde is formed in the reaction of ethanolamine with photoexcited nitrobenzene in isopropanol [17].

One may draw the conclusion that, whereas certain additives such as cysteine hydrochloride [9] tend to stabilize coumarin laser dyes under lasing

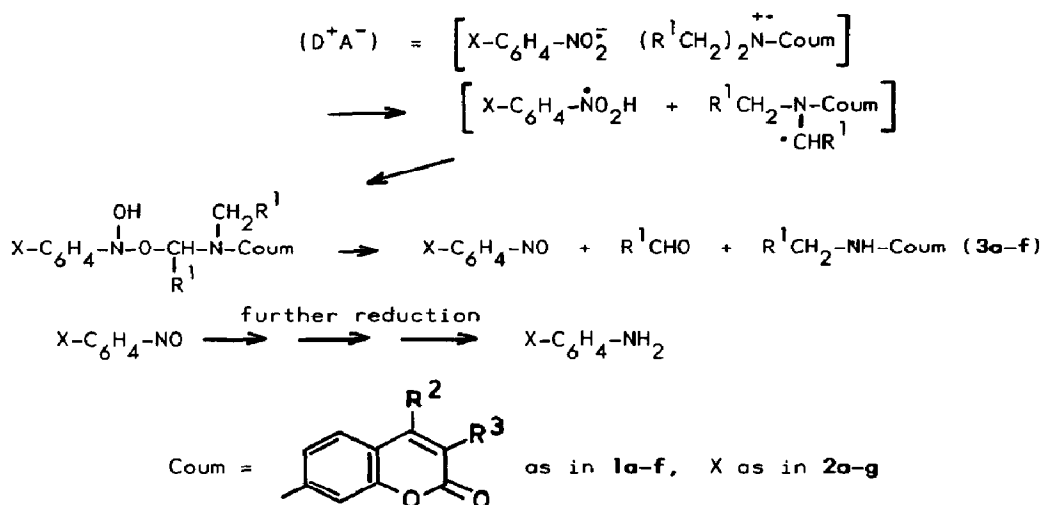


Fig. 4. Dealkylation reactions.

conditions, contaminants with electron acceptor properties, such as nitroaromatics, may be detrimental for coumarin photostability under certain specific conditions.

Acknowledgment

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