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PHOTOREACTIONS OF AROMATIC COMPOUNDS XXXI[1,2]

THE MULTIPLICITY OF THE REACTING SPECIES IN THE NUCLEOPHILIC PHOTOSUBSTITUTION REACTION OF m-NITROANISOLE

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Recently it was found that in several instances the direct nucleophilic aromatic photosubstitution mainly proceeds via a triplet state[3], although in a few cases a singlet mechanism seems to occur[4]. We therefore deemed it necessary to make a closer study of the nature of the reacting excited species of the well known[5] photohydrolysis of m-nitroanisole in alkaline medium using the experience and techniques nowadays available.

Sensitization

Upon irradiation of solutions of m-nitroanisole (mNA) in CH_3CN-H_2O 1:1* in the presence of NaOH and a large excess of benzophenone the formation of the product can be followed by measuring the increase of the absorption at 400-450 nm. In the presence of oxygen the rate of formationof the product is diminished.

In a preparative scale experiment (153 mg mNA, 600 mg NaOH and 3 g benzophenone) only $\leq$ 2 % of the incident light (254 nm) was absorbed by mNA. The only compounds isolable after two hours irradiation (Rayonet Photochemical Reactor, 2537 lamps) were unreacted starting compound and m-nitrophenol (mNP), identified by TLC, IR and NMR and a mixed melting point; yield 80 %. Sensitization could also be affected in water-methanol (2%)[5] and water-t-butanol (5%) by application of benzophenone disulphonate as an effective water-soluble sensitizer.

Quenching

To test the influence of dissolved oxygen on the photoreaction two cells were irradiated simultaneously under identical conditions, one solution being saturated with air, the other with nitrogen; concentrations: mNA 2.10^{-4}, NaOH 10^{-2} and benzophenone (if present) 8.10^{-3} M. The results are summarized in Table I. Under these conditions no (photo)reaction of benzophenone with OH^- occurred.

Similar experiments were performed in water containing 2 % methanol. Quenching by oxygen could not be observed. Mixed solvents containing higher percentages of methanol (to dissolve the added sensitizer) gave rise to side reactions. We are inclined to conclude that the absence of quenching in water-methanol (2 %) is due to the low solubility of oxygen in this solvent.

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*Unless otherwise stated this solvent mixture was used throughout. Experimental details were the same as described elsewhere[1].

TABLE I. Quenching of the photoreaction of m-nitroanisole with hydroxide ion by oxygen in acetonitrile-water 1:1.

solution saturated with	wavelength of irradiation	benzophenone present	reaction	rate constants* in l/Mole,s
N_2	254	+	mNP formation	4.3×10^{-8}
air	254	+	no reaction	-
N_2	254	-	mNP formation	4.4×10^{-8}
air	254	-	no reaction	-
N_2	313	-	mNP formation	4.7×10^{-8}
air	313	-	mNP formation	1.4×10^{-8}

* The reaction was followed spectrophotometrically. The rate constants were calculated as described by De Jongh[5b].

The heavy atom effect found in earlier experiments[5b] could be reproduced; the photoreaction was stopped by 0.99 M NaBr. The photoreaction of mNA (2.10^{-4} M) with NaOH (10^{-2} M) was completely quenched by piperylene in concentrations $\geq 4.10^{-2}$ M. In qualitative experiments it was shown that 3,3,4,4-tetramethyldiazetinedioxide (TMDD) quenches the reaction of mNA with OH^- in acetonitrile-water 1:1 as well as in water containing 2% methanol or 5% t-butanol. A series of quantum yield measurements with varying concentrations TMDD was performed in water-t-butanol (5%) under oxygen free conditions. The method of quantum yield determination described by De Jongh[5b] was adopted. The results are summarized in Table II. The relatively poor solubility of TMDD precluded measurements at concentrations > 10^{-2} M.

TABLE II. Quantum yield of the photoreaction of m-nitroanisole (2.10^{-4} M) with hydroxide ion (10^{-2} M) in water-t-butanol (5%) in the presence of various concentrations of 3,3,4,4-tetramethyldiazetinedioxide.

quencher concentration (in 10^{-2} M)	quantum yield
0	0.34
0.17	0.32
0.33	0.28
0.50	0.25
0.67	0.22
1.00	0.19

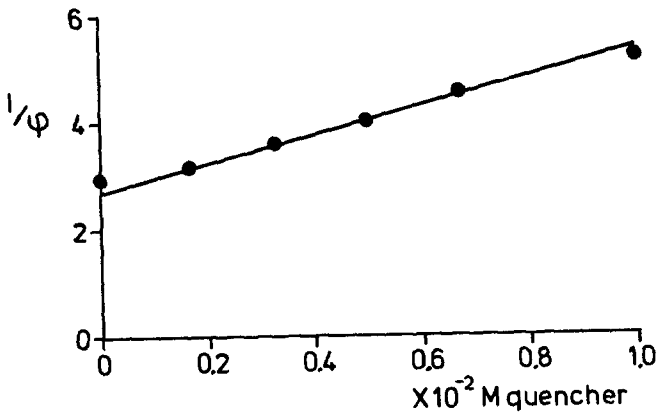

Figure I. Relation between $1/\phi$ and the concentration of 3,3,4,4-tetramethyldiazetinedioxide of the photoreaction of m-nitroanisole with hydroxide ion (10^{-2} M), wavelength 313 nm.

The plot of $1/\phi$ versus concentration of TMDO (Fig.I) yields a straight line with respective values of 250 l/Mole and 2.7 for slope and intercept. Assuming the quenching to be diffusion controlled, the lifetime τ (in 10^{-2} M NaOH and in the absence of TMDO) is calculated to be 24 ns (cf.[6]). This is in fair agreement with the lifetime of 40 ns deduced from laser photolysis measurements (in the presence of 4.10^{-2} M NaOH)[6].

Flash photolysis

Flash experiments with solutions containing mNA (2.10^{-5} M) and various nucleophiles (10^{-1} - 10^{-2} M) revealed that the formation of the photosubstitution products is finished within 20 μs (photoflash duration). The observed short lived species, λ_{max} 340-355 and 490-510 nm, therefore cannot be intermediate in the photosubstitution reaction. The lifetime of these species varies with the nucleophile used from ∿ 40 ms with OH^- to ∿ 0.3 ms with $(CH_3)_2NH$. From comparison with the data obtained by ESR we conclude the species to be the mNA radical anion.

Electron spin resonance

Irradiation of solutions containing mNA (10^{-3} M) and nucleophile (10^{-1} - 10^{-2} M) in the cavity of an ESR spectrometer yields a paramagnetic species that could be identified from the spectrum as the radical anion of mNA (coupling constants cf.[1]). This radical is also formed by electrolysis of mNA solutions containing tetraethylammonium perchlorate. It shows an absorption spectrum similar to that found in the flash experiments. The difference in lifetime of the mNA radical anion in the flash and ESR experiments may be attributed to the differences in the medium, related especially to the non-degassing of the flashed solutions.

Concluding remarks

In accord with the original assumption the high concentration of nucleophile required to achieve reaction points to a short lived intermediate excited state indeed. We now know that the triplet states of nitrobenzenes generally have very short lifetimes[7]. For m-nitroanisole (and 3,5-dinitroanisole) this was recently established in a direct way by laser-flash measurements[6]. Taking into consideration also the type of reactivity shown by the excited species, all data can be rationalized by assuming that the photosubstitution of m-nitroanisole by hydroxide ion takes its start mainly from the lowest π-π^* triplet state.

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