

PHOTOSENSITIZED NUCLEOPHILIC AROMATIC SUBSTITUTION¹

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Havinga, de Jongh and Kronenberg have suggested that photoinduced substitution reactions exhibited by many nitroaromatics proceed by attack of a nucleophile on a singlet excited state of the nitroaromatic.² The evidence cited for direct involvement of the singlet excited state is (i) lack of indications of the occurrence of triplet states or free radicals, (ii) bromide ion, which catalyzes the $S_1 \rightarrow T_1$ transition, diminishes the quantum yields of the substitution reactions, and (iii) relatively high concentrations of the nucleophile (10^{-3} to 10^{-2} M) must be present to attain appreciable rates. However, since heavy atoms such as bromine shorten the lifetime of triplet as well as singlet excited states³ and the lifetimes of nitroaromatics in the triplet state appear to be short,⁴ this evidence is not compelling and the multiplicity of the excited states involved in these substitution reactions remains an open question.

To gain further information on the nature of the excited state of the reactive nitroaromatics, we have investigated the possibility of sensitizing a nucleophilic substitution reaction. Benzophenone was selected as a sensitizer since it has a relatively high triplet energy⁵ and a large body of experimental data supports the conclusion that photochemical reactions sensitized by benzophenone in dilute solution proceed via triplet state intermediates.⁶ As substrate and nucleophile we chose 4-nitroanisole and hydroxide ion. 4-Nitroanisole is stable in aqueous alkali in the dark; however, it is readily converted to a mixture of 4-methoxyphenol (80%, nitrite displacement) and 4-nitrophenol (20%) on irradiation with ultraviolet light ($\lambda > 290 \text{ m}\mu$).⁷ This system was attractive since hydroxide is transparent and 4-nitroanisole absorbs weakly

($\log \epsilon$ 3.04 at 256 $m\mu$) in a region where benzophenone absorbs strongly (λ_{\max} 256, $\log \epsilon$ 4.30). Moreover, the reaction could be followed easily by the build-up of absorbance at 400 $m\mu$ due to 4-nitrophenoxide.

The light source was a Bausch and Lomb high intensity monochromator equipped with a 33-86-36-01 super pressure 200 w mercury lamp. A standard silica absorption cell (10 mm light path) fitted with a ground glass stopper served as a reaction vessel. It was held in a thermostatted container 2 cm from the monochromator exit slit, and the solution was stirred with a micro magnetic bar during irradiation.

Data for a series of reactions carried out with 1.0×10^{-4} M 4-nitroanisole and 1.60×10^{-2} M sodium hydroxide in aqueous *t*-butyl alcohol (2% *t*-butyl alcohol by vol.) are presented in Table I. Two of the solutions (2, 4) contained benzophenone (10^{-4} M). The solutions were saturated with either nitrogen or oxygen prior to irradiation, as indicated. In each case a band developed at 400 $m\mu$ when the solution was irradiated, and the rate of increase of absorbance at this wavelength fitted a first order rate equation.

TABLE I
Rate of Formation of 4-Nitrophenol on Irradiation of Solutions of 4-Nitroanisole and Hydroxide at 252 $m\mu$ ^a

Experiment	Benzophenone Moles/l.	Gas used to Saturate the Solution	$k_{\text{obs}} \times 10^4 \text{ sec}^{-1}$
1	0	N ₂	0.62
2	1.0×10^{-4}	N ₂	2.46
3	0	O ₂	0.77
4	1.0×10^{-4}	O ₂	0.86

^aThe band width was $\approx 15 m\mu$ (slit setting 2 on monochromator).

The significant feature of experiments 1 and 2 is that the pseudo first order rate constant for formation of 4-nitrophenol in the solution containing benzophenone (nitrogen atmosphere) is about four times greater than the rate constant for the corresponding system which lacked benzophenone. This result strongly suggests that some of the energy absorbed by benzophenone is utilized in activating 4-nitroanisole. That benzophenone indeed functions as a sensitizer for the reaction of 4-nitroanisole with hydroxide ion was confirmed by the following experiments.

Experiment 2 was repeated with the sodium hydroxide omitted. No reaction was observed; therefore, hydroxide is an essential component in the reaction system.

Experiments 1 and 2 were repeated with the monochromator set at 366 m μ , a wavelength at which 4-nitroanisole absorbs more strongly than benzophenone. A photochemical reaction occurred and 4-nitrophenol was formed; however, the rate was essentially independent of benzophenone. One may, with considerable assurance therefore, rule out the possibility that the enhanced reactivity of 4-nitroanisole in the presence of benzophenone (Exp. 2) results from formation of a complex between excited 4-nitroanisole and benzophenone which is more susceptible than excited 4-nitroanisole to attack by hydroxide.

Experiments 1 and 2 were repeated with oxygen replacing nitrogen as the saturating gas. The basis of these experiments are the observations that the benzophenone triplet is quenched by oxygen⁸ whereas photoexcited 4-nitroanisole is resistant to oxygen in aqueous solution. (In fact, the reaction of excited 4-nitroanisole with hydroxide is slightly accelerated by oxygen, probably as a consequence of oxygen intercepting an intermediate complex which would otherwise revert to hydroxide and 4-nitroanisole in the ground state.⁷) We found that the rate of reaction of 4-nitroanisole excited by light at 252 m μ is slightly accelerated by oxygen (see Exp. 3, Table I), in agreement with data for irradiations carried out at longer wavelength (>290 m μ).⁷ On the other hand, the reaction of 4-nitroanisole in the system involving benzophenone is strongly inhibited by oxygen (compare Exp. 4 and 2, Table I). These experiments clearly demonstrate that the formation of nitrophenol in Exp. 2 is directly coupled to the excitation of benzophenone.

In accord with these data and with the known properties of the excited states of benzophenone,⁶ we conclude that 4-nitroanisole is raised to the triplet excited state by interaction with triplet benzophenone, and that the triplet excited state of 4-nitroanisole is an intermediate in the pathway to 4-nitrophenol in the photosensitized reaction.

The products from the photosensitized reaction (2) and the reaction involving direct excitation (1) are the same, as evidenced by paper chromatography (4-methoxyphenol and 4-nitrophenol were obtained in each case), by nitrite analysis,⁹ and by the final absorbance values at 400 m μ ($A_{\infty} = 0.385$ in both cases, indicating that the same amount of 4-nitrophenol had been formed). This result suggests that the triplet excited state of 4-nitroanisole may be an intermediate in the reaction in which 4-nitroanisole is activated by absorption of light as well as in the photosensitized reaction.

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