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PHOTOREACTIONS OF AROMATIC COMPOUNDS – XXIX[1]

PATHWAY AND INTERMEDIATES OF THE PHOTOREACTIONS OF 3,5-DINITROANISOLE WITH NUCLEOPHILES*

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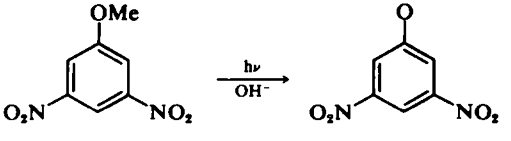
Abstract – The photoreactions of 3,5-dinitroanisole with nucleophiles (mostly hydroxide ion) have been studied by sensitization and quenching as well as by flash photolysis experiments. The photosubstitution starts mainly from the π–π^* triplet excited state (λ_{max} ~ 475 nm; τ ~ $5\cdot10^{-8}$ s or shorter depending on the concentration of nucleophile). The formation of substitution product is completed within ~ 10^{-6} s. The occurrence of the radical anion (λ_{max} ~ 550 nm; τ ~ 10^{-2}–10^{-4} s depending on the nature of the nucleophile) could be established. This cannot be intermediate in the photosubstitution reaction but is so in the formation of reduction products. The radical anion and, probably also, the substitution product seem to originate from a complex (λ_{max} ~ 410 nm; τ ~ $5\cdot10^{-7}$ s) between the triplet excited aromatic compound and its nucleophilic reaction partner. The formation of this complex is a very fast process.

INTRODUCTION

In order to obtain more detailed information about the mechanism of the nucleophilic aromatic photosubstitution we performed a kinetic and flash photolytic study of the reaction of 3,5-dinitroanisole (dNA) with nucleophiles, in particular hydroxide ion. This system was chosen because of the high quantum yield and the cleanliness of its reaction (with hydroxide ion) to 3,5-dinitrophenolate anion (dNP^-)[2,3]. Moreover, preliminary flash photolytic experiments had shown the existence of short lived, as yet unidentified, species.[4]



Experimental details

A 1 : 1 mixture of acetonitrile and water was used throughout as solvent, unless otherwise stated. Small scale reactions were performed in spectrophotometer cells; reactions on preparative scale were carried out in a photochemical reactor (Rayonet, 2537 A lamps).

Quantum yields were determined according to De Jongh,[5] with dNA ($10^{-3} - 10^{-4}$ M) and NaOH (0·025 M) and λ = 366 nm (Bausch & Lomb High Intensity Monochromator with Hanovia HP 100 Hg lamp).

In the flash experiments (discharge energies 1500–2000 Joule, duration ~ 20 μs) the concentration of dNA was $10^{-4} - 10^{-5}$ M and of nucleophile 0·5–0·005 M.

In the laser experiments dNA ($4\cdot10^{-4}$ M) and NaOH (0·04 M) were irradiated with the frequency doubled pulse (width 6 ns, energy 5% of total 2 Joule at 347 nm) of a ruby laser (Laser Associates).

The ESR spectra (Varian E3 spectrometer) were run in N_2 saturated solns of aromatic compound (~ 10^{-3} M) and nucleophile (0·05–0·1 M). Irradiation in the cavity was done with a high pressure Hg arc (Philips SP 1000) via a $NiSO_4$ soln filter. In the electrolysis experiments the Pt cathode was placed in the cavity, tetraethylammoniumperchlorate was used as electrolyte and electric currents were in the order of 10–250 μA.

Sensitization and quenching. Irradiation of a soln (1·5 l) containing dNA (100 mg), NaOH (1·5 g) and benzophenone (3 g) yielded dNP^- as the only isolable product, at least 98% of the absorption being due to benzophenone. This result indicates that the reaction may proceed via a triplet excited state of dNA.

From the absorption spectrum of dNA in solvents of different polarity it can be concluded that in the excited singlet manifold n-π^* and π-π^* states are close lying. Since the singlet-triplet splitting of π-π^* states is known to be greater than that of n-π^* states, the lowest triplet state is likely to have π-π^* character.

In order to support these conclusions we measured the quantum yield in dependence of the concentration of added 9-fluorenone (Table 1). This compound has a triplet energy of 53 kcal/Mole, probably lower than the triplet energy of dNA which may be of the same order of magnitude as

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*The investigations are described (in Dutch) in greater detail in: G. P. de Gunst, thesis, Leiden (1971).

Table 1. Quantum yield of the photoreaction of 3,5-dinitroanisole with hydroxide ion in the presence of 9-fluorenone, λ = 366 nm

Concentration 9-fluorenone (10^{-4} M)	Quantum yield
0	0·51[5]
1·4	0·51
2·1	0·49
3·6	0·49
7·0	0·41
10·5	0·38
14·0	0·35
21·0	0·30

Table 2. Lifetime of the absorption at 550–570 nm in the presence of various nucleophiles

Nucleophile	Lifetime (in ms)
OH^-	40
H_2O*	12
$(HOC_2H_4)_2NH$	8
NH_3	2
$MeNH_2$	1·5
OCN^-	1
Me_2NH	0·5
Me_3N	0·2
NCS^-	0·1
MeO^-†	0·3

*In a mixture of acetonitrile and water 1 : 9
†in methanol

the triplet energy of meta nitroanisole (60 kcal/Mole from phosphorescence measurements[6]).

Plotting the reciprocal value of the quantum yield versus the concentration of the quencher (Fig 1) gives a straight line with a slope of 670 l/Mole and a value for the intercept of 1·9. From the formula slope/intercept = $k_q.\tau$ we calculated the lifetime* of the quenched excited state in the absence of quencher, but in the presence of the nucleophile (0·025 M NaOH). Assuming that the quenching is diffusion controlled, $k_q = k_d = 1{\cdot}3 \times 10^{10}$ l/Mole,s (calculated with the modified Debije formula[7]), the lifetime $\tau = 27$ ns.

Flash photolysis. Flash excitation of solutions of dNA in the presence of nucleophiles leads to the formation of a short lived species ($\lambda_{max} \sim 550$–570 nm, Fig 2, curve a). The lifetime of the species varies from ~ 0·1–40 ms depending on the nature of the nucleophilic reagent (Table 2).

In solvent mixtures containing > 50% water the addition of a nucleophile is no longer required since water takes over this role. Addition of a nucleophile to these solvents results in a decay pattern which is no longer first order.

Spectra recorded one minute after the exciting flash shows an absorption at 400–410 nm due to the photosubstitution product dNP^-. Such an absorption is also present in the spectrum taken 20 μs after the flash. The 550–570 nm species therefore cannot be an intermediate in the nucleophilic phot substitution reaction.

Electron spin resonance. Irradiations of solns of dNA and nucleophilic reagent in the cavity of an electron spin resonance spectrometer produces radicals showing only one nitrogen coupling constant. The absence of the second nitrogen coupling constant seems a phenomenon generally encountered in protic solvents.[8–11] The spectrum of the radical only slightly changes with different nucleophiles.

When radicals are produced electrochemically again only one nitrogen coupling constant is found.

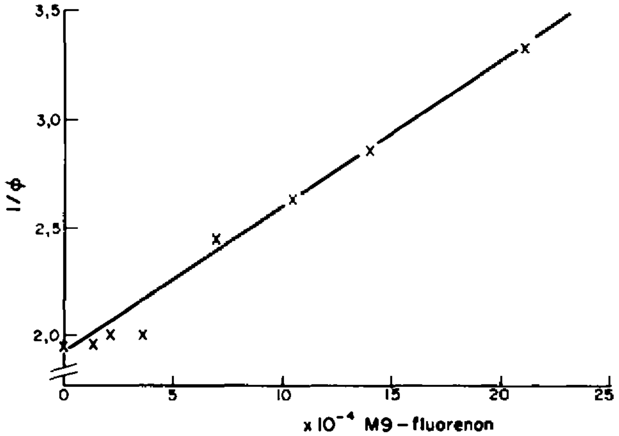

Fig 1. Relation between 1/Φ and the 9-fluorenone concentration of the photo-reaction of 3,5-dinitroanisole with hydroxide ion (0·025 M), λ = 366 nm.

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*The lifetime is defined throughout as the period in which the concentration of the disappearing species has decreased to the 1/e part of the initial value.

These radicals differ slightly from the photochemical ones, which may be due to differences in the pattern of consecutive reactions. When electrolysis is performed in an aprotic solvent, such as acetonitrile, the two expected nitrogen coupling constants appear in the spectrum indeed. The radicals thus produced can be identified as the radical anions of the respective aromatic nitrocompounds. They have lifetimes in the order of minutes in nitrogen saturated solutions. With mononitrocompounds the radical anions electrochemically produced in both protic and aprotic media are similar. A summary of the results is given in Table 3.

When the radical anion of dNA is generated electrochemically in the optical path of an absorption spectrophotometer it is possible to measure its absorption spectrum ($\lambda_{max} \sim 550$–560 nm, Fig 2, curve c). We conclude that the 550–570 nm species seen in the flash experiments is the radical anion of dNA. The difference in lifetime of the radical anion in the flash experiments versus that of the electrochemical one is probably brought about by scavenging by oxygen present in the flashed solutions and to interaction with proton donating solvents. The latter factor is possibly also responsible for the lack of measurable quantities radical anions in solutions containing water or other proton donating solvents.

Our conclusions are substantiated by the formation of 3,3′-dimethoxy-5,5′-dinitroazoxybenzene on electrolysis of dNA in acetonitrile-water (1 : 1). This clearly indicates the pathway, starting from the dNA radical anion, via proton abstraction from a protic solvent, to reduction products (*cf*[9, 12]).

With the dNA radical anion photochemically formed we deal with photoreduction of an aromatic nitrocompound from the π-π* triplet state. Although usually the n-π* triplet state is more liable to photoreduction, other examples of π-π* triplet reductions are known.[13]

Laser photolysis. Upon irradiation of solutions of dNA and hydroxide ion with a frequency doubled ruby laser pulse we observed two short lived species:

1. 412 nm species, $\lambda_{max} \sim 412$ nm, lifetime 500 ns
2. 475 nm species, $\lambda_{max} \sim 475$ nm, lifetime ~ 12 ns.

During the decay of the 412 nm species an absorption at ~ 512–550 nm is building up. An isosbestic point is observed at ~ 535 nm (Fig 3). It should be noted that the spectra in Fig 3 are constructed from measurements at 25 or 12 nm intervals. The increase in optical density of the solution continues till about 1·5 μs after the pulse, remaining then constant (at 512–550 nm) up to the maximum measure time (10 μs). We think this last absorption to be due to the radical anion of dNA (Fig 2, curve b), formed from the 412 nm species.

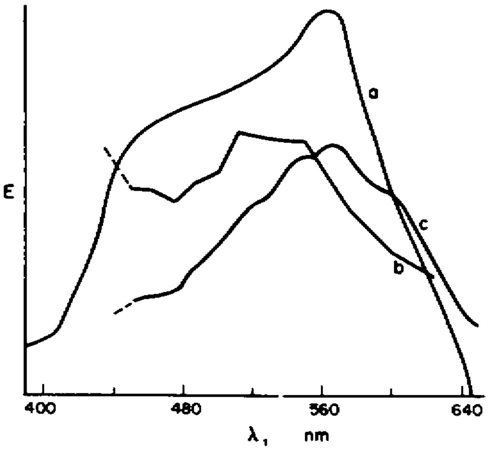

Fig 2. Absorption spectrum of 3,5-dinitroanisole radical anion, produced by: (a) irradiation with 20 μs discharge flash in alkaline medium, (b) irradiation with a frequency doubled ruby laser pulse (347 nm, 6 ns) in alkaline medium, (c) electrolysis in the presence of tetraethylammonium-perchlorate in acetonitrile.

Table 3. ESR coupling constants of radicals of some aromatic nitrocompounds, produced photochemically and electrochemically in protic and aprotic media

			Coupling constants (in Gauss)					
Aromatic compound	Solvent	Method	$a_N(1)$	$a_N(2)$	a_{H2}	a_{H4}	a_{H5}	a_{H6}
3,5-Dinitroanisole	$CH_3CN—H_2O$	photo	12·2	0	3·56	3·56	—	3·08
3,5-Dinitroanisole	$CH_3CN—H_2O$	electro	13·4	0·41	3·25	3·25	—	3·25
3,5-Dinitroanisole	CH_3CN	electro	4·41	4·41	4·41	2·63	—	4·41
m-Dinitrobenzene	$CH_3CN—H_2O$	photo	12·5	0	3·37	3·37	1·08	3·37
m-Dinitrobenzene	$CH_3CN—H_2O$	electro	13·5	0·4	3·27	3·27	1·00	3·27
m-Dinitrobenzene	CH_3CN	electro	4·56	4·56	3·06	4·13	1·06	4·13
m-Nitroanisole	$CH_3CN—H_2O$	photo	13·3	—	3·31	3·31	1·09	3·56
m-Nitroanisole	$CH_3CN—H_2O$	electro	13·2	—	3·40	3·40	1·10	3·40
m-Nitroanisole	CH_3CN	electro	10·2	—	3·54	3·54	1·06	3·81

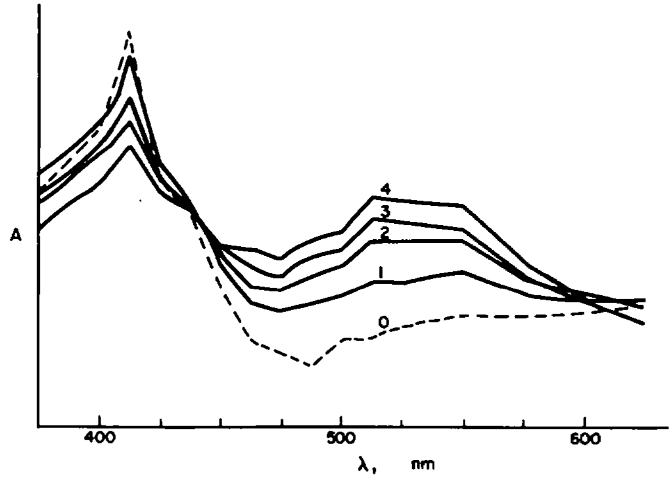

Fig 3. Absorption spectra of a solution of 3,5-dinitroanisole and hydroxide ion at different time intervals after irradiation with a frequency doubled ruby laser pulse, 0 = 0, 1 = 200, 2 = 400, 3 = 600 and 4 = 900 ns.

After 1·5 μs there is no decay of the 412 nm absorption any more. The optical density of the solution is higher then before the pulse due to the formation of photosubstitution product: dNP^- has $\lambda_{max} = 400$–410 nm. Although the direct formation of dNP^- from the 412 nm species thus cannot be observed, we propose this pathway as the most plausible.

In the absence of hydroxide ion neither the 412 nm species, nor the formation of the radical anion, nor that of the photosubstitution product was found. We conclude that the 412 nm absorption is due to an "aromate-nucleophile-complex" which may decay to ground state dNA, to photosubstitution product or to the radical anion.

For the 475 nm species the presence of a nucleophile is not necessary, be it that in the absence of hydroxide ion the lifetime is longer: 55 ns. We hold this species, with its lifetime in the same order of magnitude as the lifetime of the quenched excited state (vide supra) to be the triplet state of dNA. The difference in lifetime with varying concentrations of nucleophile can be ascribed to quenching by this reagent. When the lifetime of 55 ns is taken to be $1/k^{*}_{T_1-S_0}$ we are able to calculate the sum of $k^{*}_{qOH^-}$ and $k^{*}_{rOH^-}$ from $\tau = 1/(k_{T_1-S_0} + k_{qOH^-} + k_{rOH^-}) = 27$ ns. We find $k_q + k_r = 8 \cdot 10^8$ 1/Mole,s which is remarkably fast: only one order of magnitude lower than the rate constant of a diffusion controlled process.

CONCLUSION

The nucleophilic aromatic photosubstitution of 3,5-dinitroanisole is a very fast process: the total interaction rate constant of the reactive excited state with nucleophiles is only one order of magnitude lower than the rate constant of diffusion controlled processes in the solvent used (the quenching being assumed as diffusion controlled).

From quenching and sensitization experiments it is concluded that the reactive excited state is the π-π^* triplet state of 3,5-dinitroanisole. For this state the following lifetimes are found: 27 ns from quenching data (in the presence of 0·025 M NaOH), 12 ns from laserphotolysis experiments (in the presence of 0·04 M NaOH) and 55 ns from laser experiments in the absence of nucleophile.

The interaction between excited aromatic compound and nucleophilic reagent leads to the formation of an aromate-nucleophile-complex which is intermediate in the formation of the radical anion and probably also in the formation of the photosubstitution product. The radical anion is not an intermediate in the photosubstitution, but is so in the photoreduction.

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REFERENCES

[1] XXVIII: C. M. Lok, M. E. den Boer, J. Cornelisse and E. Havinga, *Tetrahedron* 29, 867 (1973)

[2] D. F. Nijhoff, thesis, Leiden (1967)

[3] E. Havinga and R. O. de Jongh, *Bull. Soc. Chim. Belg.* 71, 803 (1962)

[4] J. Cornelisse and E. Havinga, *Tetrahedron Letters* 1609 (1966)

[5] R. O. de Jongh, thesis, Leiden (1965)

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[*] $k_{T_1-S_0}$ rate constant for all monomolecular triplet decay processes. k_{qOH^-} rate constant for quenching of the triplet state by hydroxide ion. k_{rOH^-} rate constant for reaction of the triplet state with hydroxide ion (formation of the aromate-nucleophile-complex).

[6] J. G. Lammers, unpublished results
[7] A. Beckett, A. D. Osborne and G. Porter, *Trans. Faraday Soc.* **60**, 873 (1964)
[8] G. P. de Gunst, thesis, Leiden (1971)
[9] T. E. Gough and J. M. Cross, *J. Chem. Soc.* (B) 798 (1968)
[10] R. L. Ward, *J. Chem. Phys.* **32**, 410 (1960)
[11] P. B. Ayscough, F. P. Sargent and R. Wilson, *J. Chem. Soc.* 5418 (1963)
[12] I. R. Bellobono, A. Gamba, G. Sala and M. Tampieri, *J. Am. Chem. Soc.* **94**, 5781 (1972)
[13] S. G. Cohen, G. A. Davis and W. D. K. Clark, *Ibid.* **94**, 869 (1972)