$$2k_H\int_0^\infty(\text{IIIa})dt + k_H\int_0^\infty(\text{IIIb})dt - 2k_{H'}\int_0^\infty(\text{IVa})dt - 2k_S\int_0^\infty(\text{IVa})dt = 0$$

$$k_{H'}\int_0^\infty(\text{IVa})dt + 2k_{H'}\int_0^\infty(\text{IVb})dt - 2k_H\int_0^\infty(\text{IIIb})dt - 2k_S\int_0^\infty(\text{IIIb})dt = 0$$

$$k_H\int_0^\infty(\text{IIIb})dt - 2k_{H'}\int_0^\infty(\text{IVb})dt - 2k_S\int_0^\infty(\text{IVb})dt = 0$$

Replacing the integrals by the symbols S_{IIIa}, S_{IVa}, S_{IIIb}, and S_{IVb} and solving the six simultaneous equations by elimination of these integrals will give

$$k_{H'}/k_S = 2m_7(m_3 - m_7)$$

and

$$k_H/k_S = 2(m_3 + m_7)/(m_5 - m_3)$$

Acknowledgments. This paper and the preceding one were written in the laboratory of Professor P. D. Bartlett during a sabbatical leave of C. C. L. Valuable suggestions relating to the interpretation of the results made by Professor Bartlett and by members of his research group, particularly E. Sohl, are gratefully acknowledged. Private communications from Professor C. J. Collins which elaborated on the Collins–Lietzke treatment and made known to us the progress of some of Professor Collins' current work on labeled norbornyl systems are highly appreciated.

Photoreactions of Nitroanisoles with Cyanide Ion. Studies of Products and Reaction Sequence[1]

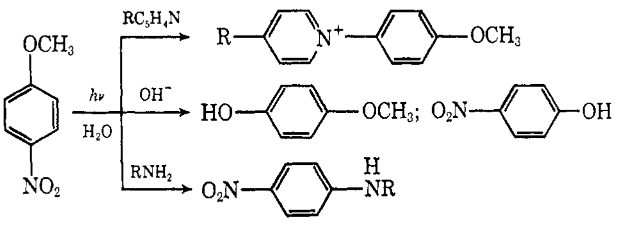
Robert L. Letsinger and James H. McCain

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received April 1, 1969*

Abstract: Irradiation of an aqueous solution of 4-nitroanisole and potassium cyanide in the presence of air affords 2-cyano-4-nitroanisole. Under the same conditions 2-nitroanisole gives a mixture of 4-cyano-2-nitroanisole and 6-cyano-2-nitroanisole, and 3-nitroanisole gives 3-nitrobenzonitrile. The preferred point of attack is therefore *meta* to nitro in each instance. The course of the reaction of 4-nitroanisole was probed by investigating the effect of oxygen on the system, possible interactions of cyanide with ground-state 4-nitroanisole, and rates and quantum yields as a function of cyanide concentration. It was concluded that cyanide intercepts photoexcited 4-nitroanisole with high efficiency, forming an intermediate of short lifetime which is oxidized by molecular oxygen to 2-cyano-4-nitroanisole. Competition experiments utilizing cyanide with pyridine, 2,4,6-trimethylpyridine, and iodide provide evidence that pyridine and cyanide compete for the same excited species of 4-nitroanisole, that pyridine converts the excited species to ground-state 4-nitroanisole (as well as yielding substitution products), that the quenching reaction is subject to steric hindrance, and that iodide quenches excited 4-nitroanisole. Data from these experiments in conjunction with data from previous studies are used to construct a table of relative reactivities for several nucleophiles toward photoexcited 4-nitroanisole.

4-Nitroanisole is inert toward common nucleophilic reagents in aqueous solution. On irradiation with ultraviolet light, however, it reacts readily with a variety of substances. With pyridine and 4-methylpyridine it affords N-(4-methoxyphenyl)pyridinium salts,[2] with hydroxide it yields 4-nitrophenoxide and 4-methoxyphenoxide,[2,3] and with alkylamines it gives the corresponding N-alkyl-4-nitroanilines,[4] as shown in Scheme I.

Scheme I



A survey of other nucleophiles revealed that cyanide ion is also highly reactive and that the course of the photochemical reaction of cyanide with 4-nitroanisole is quite different from that of the other nucleophiles. The present paper reports a detailed study of the cyanide reaction and describes competition experiments which bear on the general mechanism of reaction of nucleophiles with photoexcited 4-nitroanisole.[5]

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[1] This research was supported by a research grant from the National Science Foundation and by a Public Health Service Predoctoral Fellowship awarded to J. H. M. Part VII in series of Photoinduced Substitution. For Part VI see R. L. Letsinger and K. E. Steller, *Tetrahedron Lett.*, 1401 (1969).

[2] R. L. Letsinger, O. B. Ramsay, and J. H. McCain, *J. Amer. Chem. Soc.*, **87**, 2945 (1965); R. L. Letsinger and O. B. Ramsay, *ibid.*, **86**, 1447 (1964).

[3] S. de Vries and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **84**, 601 (1965).

[4] M. E. Kronenberg, A. van der Heyden, and E. Havinga, *ibid.*, **85**, 56 (1966).

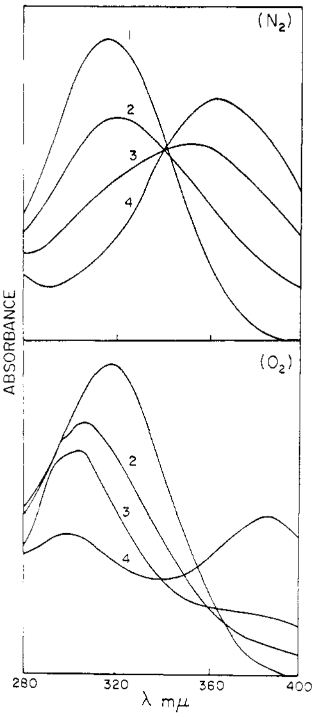
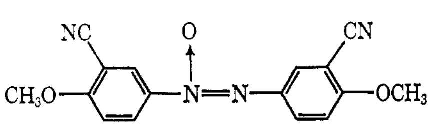


Figure 1. Absorption spectra for aqueous solution of 4-nitroanisole (1×10^{-4} *M*) and potassium cyanide (4×10^{-3} *M*) irradiated for (1) 0 sec, (2) 30 sec, (3) 110 sec, and (4) 650 sec. Upper figure (N$_2$), solution saturated with nitrogen; lower figure (O$_2$), solution saturated with air.

Results

Reaction Products. When an aqueous solution of 4-nitroanisole (1×10^{-4} *M*) and potassium cyanide (4×10^{-3} *M*) well purged with nitrogen was irradiated with ultraviolet light (λ >290 mμ), the absorption maximum at 317 mμ decreased and a new maximum developed (see Figure 1). The products were unstable and changed on standing for several hours. No immediate change occurred, however, when oxygen was admitted to the system after the irradiation period. The only substances that could be isolated from a preparative scale experiment were 3,3′-dicyano-4,4′-dimethoxyazoxybenzene (**1**, 15%) and 2-cyano-4-nitroanisole (**2**, 6%).



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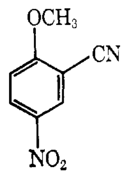
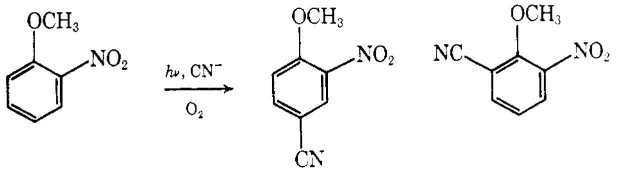


2

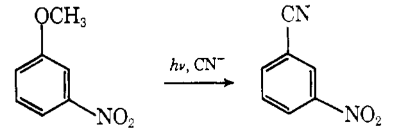
On the assumption that the initial product of the photochemical reaction had undergone some type of disproportionation, we repeated the experiment with a solution saturated with air to serve as an oxidant. The photoreaction proceeded about 30% faster than the one in the oxygen-deficient system and exhibited a different spectral pattern (Figure 1). Preparative experiments conducted with solutions saturated with air afforded 2-cyano-4-nitroanisole. None of the azoxybenzene derivative was isolated. The yield of 2-cyano-4-nitroanisole was 23% when the irradiation time was 90 min and 50% (66% based on nitroanisole consumed) when the irradiation time was 10 min. This result indicated that the cyanonitroanisole was being consumed in a secondary, slower photochemical reaction. Confirmation of the secondary reaction was obtained by directly irradiating an aqueous solution of 2-cyano-4-nitroanisole (1×10^{-4} *M*) and potassium cyanide (4×10^{-3} *M*) that had been saturated with air. The absorption maximum at 306 mμ decreased ($t_{1/2}$ = 815 sec) and an isosbestic point developed at 335.5 mμ.

The rate of the photoreaction of 4-nitroanisole with cyanide in an aqueous solution saturated with air was then followed by the decrease in absorbance at the isosbestic point for the secondary reaction (335.5 mμ). Under these conditions a simple first-order rate of decrease of absorbance was observed. The rate constant for reation of 4-nitroanisole was 16 times that for reaction of 2-cyano-4-nitroanisole under the same conditions. Consequently a good yield of 2-cyano-4-nitroanisole could be obtained by suitably controlling the irradiation time. Small-scale experiments showed that at least 90% of the 4-nitroanisole which reacts initially is converted to 2-cyano-4-nitroanisole.

2-Nitroanisole resembled 4-nitroanisole in the photochemical reaction with cyanide. On irradiation in the presence of air it was converted to 4-cyano-2-nitroanisole (**3**) and 6-cyano-2-nitroanisole (**4**) in yields of 29% and 26%, respectively. 3-Nitroanisole also showed preference for attack at a position *meta* to nitro, affording 3-nitrobenzonitrile (**5**, 46%) by displacement of methoxide. This reaction does not require an oxidation step, and it was found that oxygen did not influence the reaction as judged by the spectral changes.



3 **4**



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For investigation of the mechanism of the photoinduced substitutions attention was focused on 4-nitroanisole. Experiments were designed to provide information about the sequence of steps leading to 2-cyano-4-nitroanisole and the relative reactivity of typical nucleophiles toward the photoexcited intermediate.

Initial Step. The initial step in the reaction of 4-nitroanisole must be absorption of light by either the aromatic or by a complex formed from the aromatic and cyanide ion. Although the latter did not appear probable, the possibility was carefully investigated since complexes between cyanide and polynitroaromatics are known[6] and at least one photochemical substitution, the displacement of nitrite from trinitrobenzene by hydroxide, has been shown to proceed by way of a ground-state complex.[7]

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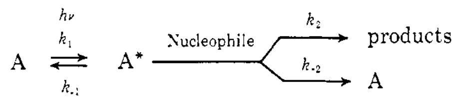
(5) For a preliminary publication see R. L. Letsinger and J. H. McCain, *J. Amer. Chem. Soc.*, **88**, 2884 (1966).

(6) R. Foster and D. Ll. Mannick, *Nature*, **171**, 40 (1953).

Three lines of evidence serve to rule out such a complex for the reaction of 4-nitroanisole. (1) The spectrum of 4-nitroanisole was unaffected when potassium cyanide was added to the solution, even at concentrations as high as 1 *M*. In general a new band develops when an aromatic forms an addition complex.[7,8] (2) 4-Nitroanisole did not migrate when an aqueous solution containing it and potassium cyanide (1.0 *M*) was subjected to electrophoresis. Since an adduct of cyanide and 4-nitroanisole would be negatively charged, a complex formed from the two would migrate in an electric field. (3) The quantum yield is sufficiently high (see later results) that the concentration of a complex would have to be high, well above the limits detectable by the above tests, if the photoreaction proceeded through the complex. We therefore conclude that the initial step in the photochemical reaction of 4-nitroanisole with cyanide, as with hydroxide and pyridine[2,9] is absorption of light by the nitroaromatic, and that the ensuing reaction involves direct attack of the nucleophile on an activated form of the nitroaromatic.

Rates and Quantum Yields. Subsequent steps in the reaction sequence were probed by investigating the effect of changes in cyanide concentration on the rate and quantum yield of disappearance of 4-nitroanisole.

Rate data for reactions carried out at 26° and 3° at pH 9.8 in the presence of air are presented in Figure 2. As shown, plots of the reciprocal of the pseudo-first-order rate constant *vs.* the reciprocal of the nucleophile concentration are linear. The reaction of cyanide therefore follows the same kinetic pattern as the reactions of pyridine and hydroxide, for which sequence 1 was proposed.[2] With the assumption of a steady-state concentration of the activated aromatic (A*), the observed rate constants may be expressed by eq 2, where k_1, k_{-1}, k_2, and k_{-2} are rate constants, respectively, for excitation of the aromatic, for spontaneous and solvent-induced deactivation processes, for nucleophile–excited-state interactions which are chemically productive, and for nucleophile–excited-state interactions which only return the aromatic to the ground state.[2]



$$\mathrm{A} \underset{k_{-1}}{\overset{h\nu,\ k_1}{\rightleftharpoons}} \mathrm{A^*} \xrightarrow{\text{Nucleophile}} \begin{cases} \xrightarrow{k_2} \text{products} \\ \xrightarrow{k_{-2}} \mathrm{A} \end{cases} \qquad (1)$$

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{k_1}\left(1 + \frac{k_{-2}}{k_2}\right) + \frac{k_{-1}}{k_1k_2[\text{Nucleophile}]} \qquad (2)$$

For evaluation of the ratios k_{-2}/k_2 and k_{-1}/k_2, information on the magnitude of k_1 is needed. This was obtained by determining quantum yields for the reaction of 4-nitroanisole with cyanide at several cyanide concentrations. The data are listed in Table I and are shown in Figure 2 as a plot of $1/\Phi$ *vs.* $1/[\mathrm{CN}^-]$. It may be noted that the quantum yields for irradiation at 366 and 313 mμ are essentially the same.

The quantum yields are related to the rate constants by eq 3. In agreement with this expression, the quantum yield and rate data were found to be self-consistent, even though quite different light sources and reaction vessels of different geometry were utilized in the experiments. As shown in Figure 2, the two sets of data may be accommodated by a single line when $k_{\mathrm{obsd}}/\Phi = k_1$ is taken to be 0.104 sec^{-1}. This value of k_1 may be used to evaluate quantum yields from rate data for reactions of 4-nitroanisole with other nonabsorbing nucleophiles studied in the same system. Values thus obtained are designated as k_{obsd}/k_1 to indicate the nature of the experimental observations.

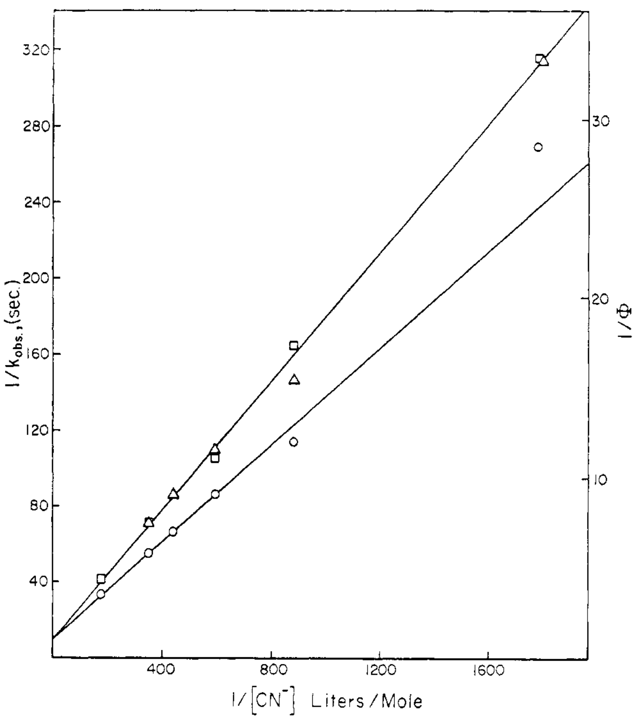


Figure 2. Photoreaction of 4-nitroanisole (1×10^{-4} *M*) with potassium cyanide in water saturated with air. Read $1/k_{\mathrm{obsd}}$ on left ordinate for rate data at 3°, ○, and at 26°, □. Read $1/\Phi$ on right ordinate for quantum yield data at 26°, △.

Table I. Quantum Yields for Reaction of 4-Nitroanisole with Cyanide in Water at 26°

$10^3 \times$ added KCN, *M*	λ of exciting light, mμ	Φ
0.784	313	0.030
1.57	313	0.065
2.35	313	0.086
3.14	313	0.11
3.92	313	0.14
3.92	366	0.13

$$k_1/k_{\mathrm{obsd}} = 1/\Phi = 1 + \frac{k_{-2}}{k_2} + \frac{k_{-1}}{k_2(\text{nucleophile})} \qquad (3)$$

The reaction of 4-nitroanisole with cyanide proceeded more rapidly at 3° than 26°. In terms of eq 3 this decrease in rate may be attributed to a decrease in k_{-1}/k_2 (a decrease of 24% for this temperature range) since the intercepts in the rate plots, and therefore k_{-2}/k_2, are the same for the experiments at both temperatures.

The intercept for the plot of $1/\Phi$ *vs.* $1/[\mathrm{CN}^-]$ is close to unity (Figure 2). Accordingly, k_{-2}/k_2 for the cyanide

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(7) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1687 (1964).

(8) R. Foster, *Tetrahedron*, **10**, 96 (1960).

(9) Additional evidence against involvement of ground-state complexes of hydroxide and pyridine is that unreasonably high equilibrium constants for formation of the complexes (K = 25–30 l./mol) would have to be assumed to account for the observed curvature in plots of k_{obsd} *vs.* nucleophile concentration. For the favorable case of hydroxide reacting with 1,3,5-trinitrobenzene, K is of the order of only 2.7 l./mol.[7]

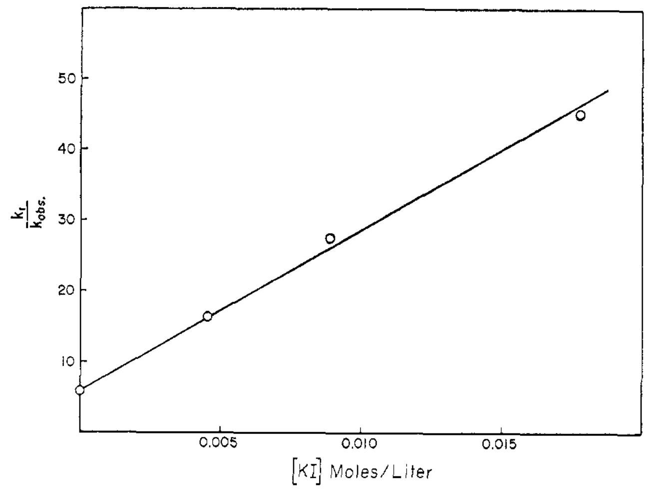

Figure 3. Photoreaction of 4-nitroanisole (1×10^{-4} *M*) and potassium cyanide (3.92×10^{-4} *M*) in water at 3° in the presence of potassium iodide.

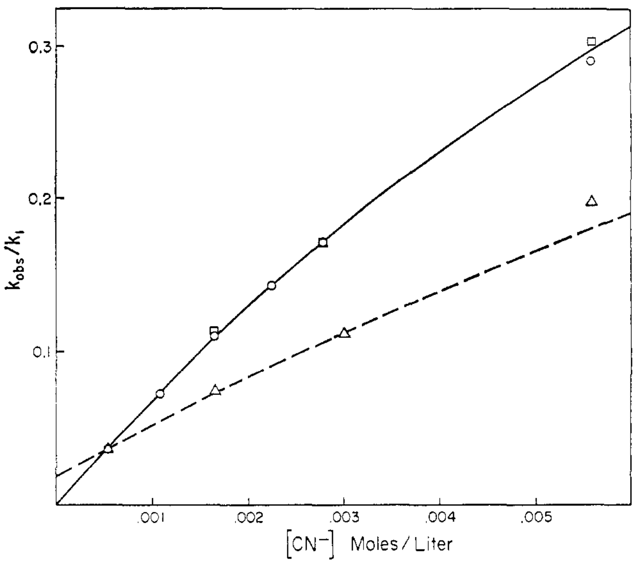

Figure 4. Pseudo-first-order rate constants for photoreaction of 4-nitroanisole (1×10^{-4} *M*) with potassium cyanide in water at 3°: no extra nucleophile, ○; with 0.04 *M* pyridine, △; with 0.04 *M* 2,4,6-trimethylpyridine, □.

reaction must be very small and a high fraction of encounters of cyanide with the excited nitroanisole must be chemically productive.

Inhibition by Iodide. 4-Nitroanisole is recovered unchanged when irradiated in aqueous solution in the presence of halide ions; that is, k_2 for reaction of halide ions with photoexcited 4-nitroanisole is zero. That some type of interaction may take place, however, is shown by the fact that chloride and bromide ions in high concentration inhibit photoreactions of nitroaromatics with other nucleophiles.[10] As a measure of reactivity of a nucleophile which yields no substitution product we investigated the effect of iodide on the reaction of cyanide with 4-nitroanisole. Values of k_1/k_{obsd} are plotted in Figure 3 as a function of the iodide concentration. It is apparent that iodide is an effective inhibitor of the cyanide reaction. From the slope of the line in Figure 3 and eq 4 the relative reactivity of iodide and cyanide toward photoexcited 4-nitroanisole, as measured by $k_{-2}{}^{\text{I}}/k_2{}^{\text{CN}}$, is found to be 6.3.

$$\frac{k_1}{k_{\text{obsd}}} = 1 + \frac{k_{-1}}{k_2{}^{\text{CN}}[\text{CN}]} + \frac{k_{-2}{}^{\text{I}}[\text{I}]}{k_2{}^{\text{CN}}[\text{CN}]} \qquad (4)$$

Inhibition by Pyridine. Competition experiments involving other nucleophiles are also instructive. Of particular interest is the competition between pyridine and cyanide since these substances typify the uncharged and anionic nucleophiles and their reactions represent extremes in type of substitution.

A plot of $1/k_{\text{obsd}}$ *vs.* 1/[pyridine] for reaction of pyridine with 4-nitroanisole in water at 3° yields slope and intercept values of 9.0 mol/l. and 264 sec, respectively.[2] In terms of eq 3, these values give $1 + k_{-2}{}^{\text{Py}}/k_2{}^{\text{Py}} = 27$ and $k_{-1}/k_2{}^{\text{Py}} = 0.94$ mol/l. sec on multiplication by k_1. The large intercept indicates that pyridine is an effective quencher of the excited state of 4-nitroanisole; *i.e.*, 26 encounters convert excited 4-nitroanisole to the ground state for each encounter that is chemically productive. On the assumption that pyridine and cyanide attack the same type of excited species of 4-nitroanisole, k_{-1} is independent of the nucleophile and a ratio of slopes derived from data for pyridine and cyanide gives $k_2{}^{\text{CN}}/k_2{}^{\text{Py}}$, which is a measure of the relative chemical reactivity of the two nucleophiles toward excited 4-nitroanisole. The value for this ratio was found to be 70 for reactions carried out in water at 3°.

These results lead to the prediction that pyridine should function as an inhibitor of the cyanide reaction; indeed, at appropriate concentrations, 4-nitroanisole should react more slowly with a mixture of pyridine and cyanide than with the cyanide alone. Experiments with a mixture of nucleophiles therefore provide an opportunity to test the validity of the kinetic interpretation (*e.g.*, that pyridine converts excited 4-nitroanisole to the ground state as well as displacing nitrite) and the assumption that pyridine and cyanide react with the same type of excited species.

Photoreactions were carried out at 3° with aqueous solutions containing 4-nitroanisole (1×10^{-4} *M*), pyridine (0.040 *M*), and potassium cyanide (7.84×10^{-4} to 7.84×10^{-3} *M*). The solutions were saturated with air and the reactions were followed by the decrease in absorbance at 335.5 mμ. As shown in Figure 4, these reactions were in fact slower than the corresponding reactions of cyanide in the absence of pyridine. The data therefore confirm the prediction that pyridine in low concentration inhibits the photoreaction of 4-nitroanisole with cyanide.

The dashed line in Figure 4 represents values of k_{obsd} for disappearance of 4-nitroanisole calculated by means of eq 5 and rate-constant ratios determined from the reactions involving single nucleophiles. Equation 5 corresponds to an extension of Scheme I in which two nucleophiles (pyridine and cyanide) compete for the same excited species, A*. The ratio $k_{-2}{}^{\text{CN}}/k_2{}^{\text{CN}}$ is taken to be zero. The agreement between these values and the ex-

$$k_{\text{obsd}} = \frac{k_1\left[\dfrac{k_2{}^{\text{CN}}[\text{CN}]}{k_2{}^{\text{Py}}[\text{Py}]} + 1\right]}{\dfrac{k_{-1}}{k_2{}^{\text{Py}}[\text{Py}]} + \dfrac{k_{-2}{}^{\text{Py}}}{k_2{}^{\text{Py}}} + \dfrac{(k_2{}^{\text{CN}} + k_{-2}{}^{\text{CN}})}{k_2{}^{\text{Py}}}\dfrac{[\text{CN}]}{[\text{Py}]} + 1} \qquad (5)$$

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[10] E. Havinga, R. O. de Jongh, and M. E. Kronenberg, *Helv. Chim. Acta*, **50**, 2550 (1967).

perimental points strongly supports the mechanistic model proposed and the assumptions on which it is based.

Competition between 2,4,6-Trimethylpyridine and Cyanide. Additional information on the mechanism of the nucleophilic quenching reaction was obtained by investigating quenching by 2,4,6-trimethylpyridine, both by analysis of rate data from reactions of trimethylpyridine with 4-nitroanisole and by the effect of trimethylpyridine on the reaction of 4-nitroanisole with cyanide.

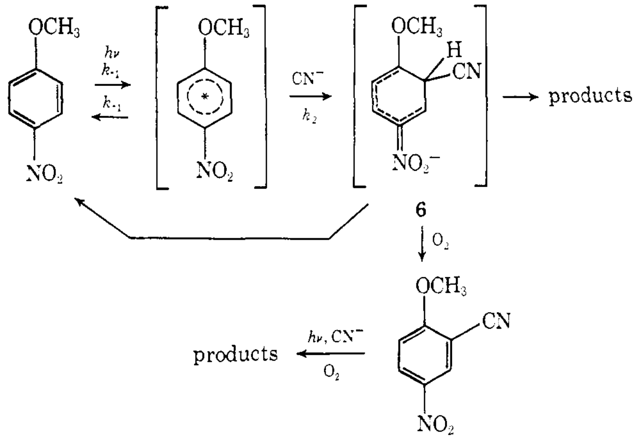
The photoreaction of 2,4,6-trimethylpyridine with 4-nitroanisole was very slow. On long irradiation, however, a pyridinium salt was formed by displacement of nitrite. Rate measurements were less reproducible than with pyridine because of the long irradiation periods required. Data for a series of reactions, however, gave intercept and slope values of ~90 and ~22 for a plot of k_1/k_{obsd} against 1/[trimethylpyridine]. With data from the pyridine reactions these yield $k_{-2}^{\mathrm{TMPy}}/k_{-2}^{\mathrm{Py}}$ ~0.14 and $k_2^{\mathrm{TMPy}}/k_2^{\mathrm{Py}}$ ~0.04 (where k^{TMPy} is a rate constant for reaction of 2,4,6-trimethylpyridine), indicating that quenching as well as substitution by the pyridines is subject to steric hindrance.

The ineffectiveness of 2,4,6-trimethylpyridine as a quencher was revealed directly by competition experiments. As shown in Figure 4, 2,4,6-trimethylpyridine at 0.04 *M* had no observable inhibitory effect on the reaction of cyanide with 4-nitroanisole, in contrast to pyridine which had a pronounced effect under the same conditions. It therefore appears that the quenching reaction must involve close contact between the nucleophile and the nitroaromatic.

Discussion

The steps in the reaction of 4-nitroanisole with cyanide deduced from this study are summarized in Scheme II.[11] Light is absorbed by 4-nitroanisole. Ultraviolet and electrophoretic experiments rule out a complex between cyanide and 4-nitroanisole in the ground state as an intermediate in the main pathway. The resulting activated species may either return to the ground state or form an adduct (**6**) with cyanide. Partitioning depends on the cyanide concentration as well as on the solvent and temperature, which influence the rate constants k_{-1} and k_2 (k_{-1}/k_2 decreases with a decrease in temperature). Intermediate **6** has a sufficiently long lifetime to react efficiently with oxygen in solution. The product of the oxidation is 2-cyano-4-nitroanisole, which may be isolated in 50% yield or better. This compound is also susceptible to photoinduced reaction with cyanide and is converted to other products if the irradiation period is extended. In the absence of oxygen, material stored as **6** in part returns to ground-state 4-nitroanisole, as shown by the slower rate of the photoreaction of 4-nitroanisole in the absence of oxygen, and in part undergoes oxidation–reduction to azoxybenzene derivatives and other substances. The disproportionation appears to be fast since admission of oxygen to the system, after irradiation has been terminated, does not afford 2-cyano-4-nitroanisole.

Scheme II



Experiments with pyridine and cyanide present simultaneously in solution provide direct evidence that pyridine quenches excited 4-nitroanisole (converts it to the ground state), a reaction postulated previously on the basis of analysis of the kinetics of displacement of nitrite from 4-nitroanisole by pyridine.[2] The quantitative agreement between the rates observed for mixtures of pyridine and cyanide and the values calculated from rate data for the individual nucleophiles support the view that pyridine and cyanide compete directly for the same excited-state species of 4-nitroanisole. The differences in the types of compounds produced by reactions of pyridine and cyanide must therefore reflect differences in the response of the nucleophiles to the excited state of the nitroanisole.

In view of these results it is reasonable to assume that other nucleophiles which act in the same concentration range and exhibit similar substitution reactions interact with the same excited state of 4-nitroanisole. Relative rate constants for the chemically productive steps (k_2) and for simple quenching steps (k_{-2}) for nucleophiles may then be derived from rate and quantum yield data, as described in detail for pyridine and cyanide in the Results section. Such values expressing relative reactivities of nucleophiles toward photoexcited 4-nitroanisole obtained from data in this and the previous paper[2] are collected in Table II. The value for iodide, which does not afford a substitution product with 4-nitroanisole, was obtained from the effect of iodide on the rate of reaction of cyanide with 4-nitroanisole. Water reacts very slowly if at all with 4-nitroanisole. The value for deactivation by water is an upper limit based on the assumption that all deactivation corresponding to k_{-1} is caused by nucleophilic attack by water (55.5 *M*).

As judged by the sum of the substitution and deactivation reactions, iodide is the most active reagent examined, even though no substitution products are formed. Cyanide is next, followed by hydroxide, 4-methylpyridine, and pyridine, which do not differ appreciably in total reactivity. 2,4,6-Trimethylpyridine is considerably less reactive in both substitution and deactivation, presumably as a consequence of the steric

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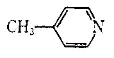
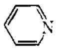
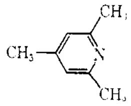
[11] Sensitization experiments with benzophenone indicate that the photoinduced reaction of 4-nitroanisole with hydroxide probably proceeds through the triplet excited state of the nitroanisole: R. L. Letsinger and K. E. Steller, *Tetrahedron Lett.*, 1401 (1969). By inference, the reaction with cyanide likewise probably involves a triplet-state intermediate. In this case a more detailed description of the photoinduced substitution would show excitation of 4-nitroanisole to the singlet excited state followed by efficient intersystem crossing to a triplet state, which either reacts directly with cyanide or affords an active metastable intermediate which reacts with cyanide. For discussion of the charge distribution in excited-state nitroaromatics see ref 10 and H. Zimmerman and S. Somasekhara, *J. Amer. Chem. Soc.*, **85**, 922 (1963).

Table II. Relative Rate Constants for Reaction of Nucleophiles with Photoexcited 4-Nitroanisole in Water at 3°

Nucleophile	Substitution reaction[a]	Deactivation reaction[b]
CN^-	70	~0
OH^-	4.5	19
	4.7	24
	1	26
	~0.04	~3
H_2O	0	<0.03
I^-	0	440

[a] $k_2^{\text{Nucleophile}}/k_2^{\text{Pyridine}}$. [b] $k_{-2}^{\text{Nucleophile}}/k_2^{\text{Pyridine}}$.

effect of the methyl groups which hinder the approach of the nucleophile to the aromatic.

The variety of types of products obtained from the photoinduced reactions of 4-nitroanisole pose an interesting problem. Why, for example, does pyridine displace the nitro group whereas cyanide adds at the carbon *meta* to nitro? An attractive explanation, compatible with the data in Table II, is that reactive nucleophiles in general tend to attack at the same position in a given molecule (subject of course to modification because of steric effects), these positions being determined by the electronic structure of the excited aromatic. The course of the reaction then depends upon the stability of the resulting intermediate and the relative leaving tendency of the nucleophile and a group which it may displace. Thus the most reactive position in 4-nitroanisole appears to be *meta* to nitro. When cyanide strikes, it forms a carbon–carbon bond and the intermediate lasts long enough to react with oxygen or to disproportionate. In contrast, the intermediate formed on addition of pyridine at the same carbon is unstable since pyridine is a good departing group. Pyridine therefore backs away and the nitroanisole returns to the ground state. Positions of secondary activity are the carbons holding the nitro and methoxyl groups. Replacement of nitro by pyridine is favorable since nitrite is a good departing group. Replacement of methoxyl by pyridine is unfavorable since methoxide is a poor leaving group relative to pyridine. As a consequence a high yield of N-(4-methoxyphenyl)pyridinium salt is formed but the quantum efficiency is low because of unproductive interactions at carbons *meta*, and to a lesser extent *para*, to the nitro group. The other reactive nucleophiles fit the same pattern.[12]

A survey of reaction products indicates that 2-nitroanisole is much like 4-nitroanisole with respect to the photoinduced substitution reactions. With 3-nitroanisole the only reactive position for substitution appears to be at carbon joined to methoxyl since hydroxide,[10] alkylamines,[10] and cyanide all displace methoxide and pyridine fails to react under conditions for which the reaction of pyridine with 4-nitroanisole is complete.[13]

Experimental Section

Ultraviolet spectra were determined with a Cary Model 11 spectrophotometer; infrared spectra were recorded on a Baird Model AB-2 spectrophotometer. A Varian A-60 spectrometer was used to obtain nmr spectra, tetramethylsilane being used as an internal standard. Melting points were determined with a Fisher-Johns apparatus, and elemental analyses were made by Micro-Tech Laboratories, Skokie, Ill.

Kinetic Runs. The reactions were carried out in a Pyrex vessel irradiated with light from a 1200-W General Electric Co. UA-11 photochemical lamp. The lamp characteristics, the geometry of the system, and the procedure for carrying out the reactions were the same as described in detail in a previous publication.[2] At the substrate concentrations employed (10^{-4} *M* for 4-nitroanisole) the absorbance changes corresponding to substrate disappearance or product appearance are well described by a first-order rate equation, unless otherwise noted. Above 10^{-3} *M*, 4-nitroanisole absorbs a high fraction of the incident light and the initial rate of reaction is essentially independent of the substrate concentration, *i.e.*, the reaction is zero order with respect to substrate. As an indication of the fraction of light absorbed under the reaction conditions, the initial rate of reaction of 4-nitroanisole at 1×10^{-4} *M* with pyridine (0.08 *M* in 22% aqueous *t*-butyl alcohol) was 38% of the initial rate of reaction of 4-nitroanisole at 2×10^{-3} *M* or higher.

The photochemical lamp was quite stable over short periods of time but the intensity gradually decreased with use. Over a period of 2 years while the data were being collected, the decrease amounted to 13% as measured by the rate of reaction of 4-nitroanisole with aqueous sodium hydroxide. Accordingly, the rate data collected at different times have been adjusted to correspond to values for the lamp in its initial condition.

Rates for reaction of cyanide with 4-nitroanisole were measured in solutions saturated with air and buffered with borate at pH 9.8 unless otherwise indicated. The cyanide ion concentrations have been corrected for hydrolysis of KCN ($[CN^-] = 0.715[KCN]$ added to the solution). The reactions were followed by the decrease in absorbance at 335.5 mμ, at which point the absorbance is not influenced by the photoreaction of 2-cyano-4-nitroanisole (a product of the reaction) with cyanide.

Quantum Yields. For quantum-yield determinations light from a Bausch and Lomb high intensity monochromator equipped with a 33-86-36-01 super pressure mercury source was employed. The monochromator was set at 313 mμ and the entrance and exit slits were set at 2 and 1 mm. Under these conditions the maximum band width was 20 mμ and most of the light was within a band of 10 mμ (as measured by a Jarrel-Ash spectrometer). The light passed directly into a standard glass-stoppered 10 × 10 mm silica cuvette which served as the reaction vessel. The cell was held 2 cm from the exit port of the monochromator in a metal compartment maintained at constant temperature by flowing water, and the reaction mixture was stirred by a small magnetic bar. Light not absorbed by the reaction solution passed into a second cuvette which contained the actinometer solution, potassium ferrioxalate trihydrate in 0.1 *N* sulfuric acid. Light incident on the reaction solution was determined by irradiating samples of actinometer solution in the reaction vessel both before and after irradiation of the reaction mixture, as described by Mason, Boekelheide, and Noyes.[14] The extent of reaction was determined by the decrease in absorbance at 335.5 mμ, and the period of irradiation was such that the reaction proceeded less than 20% to completion.

Electrophoresis Experiments. Whatman 3MM paper was spotted with samples of 4-nitroanisole, 4-nitrophenol, and 1,3,5-trinitrobenzene (the latter two compounds to serve as controls). The paper was sprayed with 1.0 *M* aqueous sodium hydroxide and placed on the plate of a Savant Flat Plate electrophoresis apparatus. Wicks of 3MM paper were saturated with the alkaline solution and placed to contact both the paper and the buffer trays, which contained 1.0 *M* sodium hydroxide. On electrophoresis at 500 V, 4-nitroanisole failed to move (showing the absence of a stable complex with hydroxide) while 1,3,5-trinitrobenzene, which is known to form a complex,[7] migrated 1.4 cm, and 4-nitrophenoxide migrated 1.6 cm.

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(12) While this interpretation is consistent with the available data, it must be recognized, of course, that other mechanisms for deactivation of the excited state of 4-nitroanisole by interaction with pyridines and with anions (especially iodide) could be operative.

(13) For a detailed discussion of the photoreaction of 3-nitroanisole with hydroxide see R. O. de Jongh and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **85**, 275 (1966).

(14) C. R. Mason, V. Boekelheide, and W. A. Noyes, Jr., in A. Weissberger, "Techniques in Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1956, p 257.

In a similar experiment the paper was sprayed with 1.0 *M* aqueous potassium cyanide. The wick and the buffer trays contained 1.0 *M* sodium hydroxide as in the previous case. 4-Nitroanisole failed to move on electrophoresis while the trinitrobenzene spread over a distance (average 1.2 cm) and the nitrophenol (ionized in the alkaline solution) moved 1.2 cm (average).

Products from 4-Nitroanisole (Nitrogen Atmosphere). A solution containing 500 mg of 4-nitroanisole and 2.0 g of potassium cyanide in 100 ml of *t*-butyl alcohol and 400 ml of water was placed in a 1 l. Pyrex vessel and flushed with a stream of nitrogen for 30 min. The vessel was capped, partially immersed in an ice bath, and irradiated with light from the GE photochemical lamp. The solution turned yellow when placed under the light and took on a reddish hue after long irradiation. After 3 hr the solution was removed, evaporated to one-half the original volume *in vacuo* at 40°, and filtered to remove the brown precipitate (**1**) which separated. Extraction of the filtrate with ether afforded a small amount of dark material which on chromatography on silica gel (2 × 20 cm; eluents: hexane, benzene, methanol) afforded 35 mg of **2** (from benzene). Some black amorphous material was obtained from the methanol solution; however, no compounds could be isolated from it.

Compound **1**, mp 224.5–225.5°, after recrystallization from benzene–heptane, showed peaks at 4.42, 6.19, 6.27, 6.71, 7.81, 8.99, and 9.83 μ in the ir region and at 229 and 344 mμ (95% ethanol) in the uv region. It was identified as 3,3′-dicyano-4,4′-dimethoxyazoxybenzene by the nmr spectrum (6H as a singlet at 3.57 ppm, 2H as a multiplet centered at 6.58 ppm, and 4H as a multiplet centered at 8.0 ppm), the analysis, and a mixture melting point with a sample of the compound synthesized independently.

Anal. Calcd for $C_{16}H_{12}N_4O_3$: C, 62.34; H, 3.90; N, 18.18. Found: C, 62.31; H, 3.92; N, 17.64.

The sample for comparison was obtained by reducing 0.50 g of 2-cyano-4-nitroanisole in 30 ml of ethanol and 2.5 ml of 10% aqueous ammonium chloride by slow addition of 1.5 g of zinc dust. The mixture was stirred for 1 hr and filtered. Evaporation of the filtrate gave 0.33 g of crystalline product, mp 136–137° (probably the hydrazo derivative), which on oxidation with sodium dichromate in aqueous sulfuric acid yielded 3,3′-dicyano-4,4′-dimethoxyazoxybenzene quantitatively. This compound had the same properties as that isolated from the photochemical reaction and the mixture melting point showed no depression.

Compound **2**, mp 127.5–128°, was shown to be 2-cyano-4-nitroanisole (lit. mp[15] 126°, 130°) by comparison with a sample prepared in 70% yield from 2-amino-4-nitroanisole by the Sandmeyer reaction by the procedure of Sannie and Lapin.[16] The two samples showed the same uv, ir, and nmr spectra (3H singlet at 4.16 ppm, 1H multiplet centered at 7.30 ppm, and 2H multiplet centered at 8.60 ppm) and the mixture melting point showed no depression.

Products from Reaction of 4-Nitroanisole (Air). The reaction was carried out by the same procedure used with nitrogen except that air replaced nitrogen in the initial sweeping step and a stream of air was bubbled through the solution throughout the period of irradiation. In addition the reaction time was reduced to 1.5 hr. Work-up as in the previous case afforded 133 mg (23%) of purified 2-cyano-4-nitroanisole. From a similar experiment in which oxygen was used as the sweep gas the yield was 229 mg (39%).

In another experiment 100 mg of 4-nitroanisole and 400 mg of potassium cyanide in 20 ml of *t*-butyl alcohol and 480 ml of water in a 1-l. flask was irradiated for 10 min at ice temperature while air was bubbled through the solution. On extraction with four 200-ml portions of ether, evaporation of the ether, and elution of the residue from silica gel (2 × 20 cm) with benzene, 25.4 mg of 4-nitroanisole and 57.4 mg (50% total, 66% based on 4-nitroanisole consumed) of 2-cyano-4-nitroanisole were obtained. The yields of 4-nitroanisole and cyanonitroanisole were 21.5 mg and 61.2 mg (53% total, 68% based on 4-nitroanisole consumed) when the reaction was repeated with oxygen as the sweep gas. When the experiment was repeated with nitrogen in place of air or oxygen, none of the 2-cyano-4-nitroanisole was found.

Reactions of 2-Nitroanisole and 3-Nitroanisole with Potassium Cyanide. A solution of 500 mg of 2-nitroanisole and 4.0 g of potassium cyanide in 50 ml of *t*-butyl alcohol and 450 ml of water was irradiated for 1.5 hr in a 1-l. Pyrex flask cooled in an ice bath. Oxygen was bubbled through the solution during irradiation. Near completion of irradiation a white precipitate began to form.

The solution was extracted with three 200-ml portions of ether, which were collected, dried, and evaporated. The residue was placed on a silica gel column and eluted with benzene. In succession the following compounds were recovered: 2-nitroanisole, 223 mg; 6-cyano-2-nitroanisole, 84 mg (26% based on unrecovered 2-nitroanisole), mp 103.5–104.5° from hexane (lit[17] mp 104–105°), nmr spectrum 3H at 4.26 ppm, 1H centered at 7.42 ppm, and 2H centered at 8.05 ppm; and 4-cyano-2-nitroanisole, 92 mg (29% based on unrecovered 2-nitroanisole), mp 151–152° from water (lit.[18] mp 151°), nmr spectrum 3H at 4.12 ppm and 1H each centered at 7.23, 7.96, and 8.26 ppm.

A similar reaction was carried out with 100 mg of 3-nitroanisole, 400 mg of potassium cyanide, 20 ml of *t*-butyl alcohol, and 480 ml of water. The irradiation time was 5 min. Extraction with ether and chromatography as in the previous case gave 28.4 mg of 3-nitroanisole and 32 mg (46% based on unrecovered 3-nitroanisole) of 3-nitrobenzonitrile, identified by melting point (117.5–118°; lit.[19] mp 117–118°) and infrared spectrum (comparison with Sadtler Standard Spectrum No. 17535, The Sadtler Research Laboratories, Philadelphia, Pa.).

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