

The Role of Azo-ethers in the Dediazonation of *p*-Nitrobenzenediazonium Ion in Alkaline Methanol

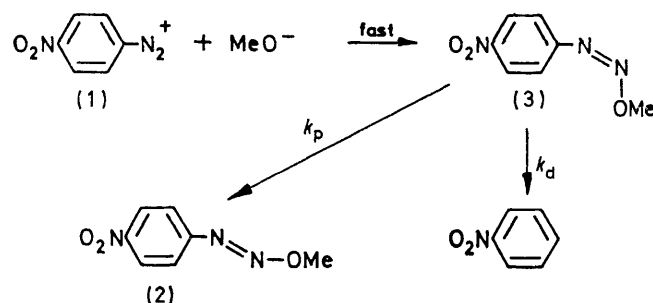
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Summary *p*-Nitrobenzenediazonium ion combines rapidly with methoxide ion to form *cis-p*-nitrophenylazo methyl ether, which then further reacts to form nitrobenzene (by a radical mechanism) and the *trans*-azo-ether in approximately equal amounts.

TREATMENT of *p*-nitrobenzenediazonium ion (1) with NaOMe in MeOH affords nitrobenzene in high yield.¹ When (1) (5×10^{-4} M) is combined with 0.1M-NaOMe in MeOH at 30°, and the rate is followed by the quenching of aliquot portions by acid and photometric determination of the dye formed upon coupling with α -naphthylamine, a procedure which determines not only (1) but anything which is converted into (1) by acid quenching, it is found that about half of the coupling capacity is destroyed within the first minute, whereas the remaining half is lost slowly according to a first-order rate law with a half life of 4.9×10^3 s. The rate of the slow phase is the same as the rate of decomposition of the isolable *p*-nitrophenylazo methyl ether (2).²

for the constituent reactions, k_d for decomposition to nitrobenzene and k_p for conversion into the "protected" for m, (2). Results are given in the Table.



SCHEME

A salient result is that both k_p and k_d are nearly independent of NaOMe concentration. This could mean either

First-order rate coefficients for the reaction of *p*-nitrobenzenediazonium fluoroborate^a with sodium methoxide in methanol

T/°C	[NaOMe]/M	% Decomposition in fast phase	k_p/s^{-1}	k_d/s^{-1}
-16.40	0.113	17.6	1.12×10^{-3}	2.39×10^{-4}
-10.80	0.113	19.5	2.12×10^{-3}	5.13×10^{-4}
-3.80	0.104	23.1	4.89×10^{-3}	1.47×10^{-3}
0	0.0032	30.2	6.28×10^{-3}	2.72×10^{-3}
0	0.0104	29.4	6.90×10^{-3}	2.87×10^{-3}
0	0.104	25.0	7.23×10^{-3}	2.41×10^{-3}
+2.50	0.103	25.2	8.56×10^{-3}	2.89×10^{-3}

^a Ca. 4.5×10^{-4} M.

That the fast phase forms nitrobenzene and (2) in virtually equal amounts was confirmed by extraction with pentane shortly after mixing. The i.r. spectrum of the extract closely resembled that of a mixture of nitrobenzene and (2) in equimolar amounts. Also, authentic (2) has been isolated as a solid from the extract.^{3,4}

By means of the technique described, the rate of the fast phase of the reaction of (1) with NaOMe was determined at lower temperatures. The "infinity" absorbance for the fast phase, estimated by extrapolation of slow-phase absorbances to zero time, was utilized for the reckoning of overall pseudo-first-order rate coefficients (k_p) in the usual way, and for splitting the k_p values into rate coefficients

(a) that methoxide ion is not a component of the rate-limiting transition states, or (b) that (1) reacts extremely rapidly and essentially quantitatively with methoxide ion to form a species which has the same methoxy content as the two rate-limiting transition states and which is reconverted into (1) on acid quenching. Because of the difficulty of visualizing a rate-limiting step between (1) and (2) that does not involve methoxide ion, the second alternative is indicated. Moreover, Ritchie and Virtanen⁵ have shown by a stopped-flow kinetic study that (1) and NaOMe react very rapidly ($k = 3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 23 °C) to form an adduct which they assume to be *cis*-azo-ether (3). This assignment is plausible by analogy with other co-ordination

reactions of diazonium ions with nucleophiles. If it is correct, the isolable azo ether is the *trans*-isomer, and the system may be represented as shown in the Scheme.

These experiments do not demonstrate whether the reactions whereby (3) is converted into nitrobenzene and (2) occur directly or *via* preliminary dissociation into diazonium ions. The activation parameters calculated from the data in the Table [ΔH^\ddagger 15 kcal mol⁻¹ and ΔS^\ddagger -14 cal deg⁻¹ mol⁻¹ for (3) \rightarrow (2), ΔH^\ddagger 19 kcal mol⁻¹ and ΔS^\ddagger -2 cal deg⁻¹ mol⁻¹ for (3) \rightarrow nitrobenzene] do not completely clarify the position.

As for the transformation of (3) into nitrobenzene, the fact that reaction in MeOD solution forms nitrobenzene

virtually free of deuterium excludes a possible mechanism *via* carbanion intermediates.⁶ Our observation that treatment of (1) with NaOMe (0.1 M) in the presence of 0.25 M-iodobenzene forms nitrobenzene and 1-iodo-4-nitrobenzene in approximately equal amounts indicates a radical mechanism⁷ and thus that a non-radical, intramolecular transformation⁴ is at most a minor reaction pathway.

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