The Role of Azo-ethers in the Dediazoniation 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 $4{\cdot}9 \times 10^3$ s. The rate of the slow phase is the same as the rate of decomposition of the isolable *p*-nitrophenylazo methyl ether (**2**).[2]

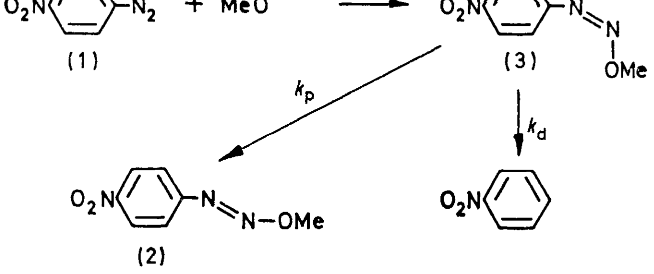
First-order rate coefficients for the reaction of p-*nitrobenzenediazonium fluoroborate*[a] *with sodium methoxide in methanol*

T/°C	[NaOMe]/M	% Decomposition in fast phase	k_p/s^{-1}	k_d/s^{-1}
−16·40	0·113	17·6	$1{\cdot}12 \times 10^{-3}$	$2{\cdot}39 \times 10^{-4}$
−10·80	0·113	19·5	$2{\cdot}12 \times 10^{-3}$	$5{\cdot}13 \times 10^{-4}$
−3·80	0·104	23·1	$4{\cdot}89 \times 10^{-3}$	$1{\cdot}47 \times 10^{-3}$
0	0·0032	30·2	$6{\cdot}28 \times 10^{-3}$	$2{\cdot}72 \times 10^{-3}$
0	0·0104	29·4	$6{\cdot}90 \times 10^{-3}$	$2{\cdot}87 \times 10^{-3}$
0	0·104	25·0	$7{\cdot}23 \times 10^{-3}$	$2{\cdot}41 \times 10^{-3}$
+2·50	0·103	25·2	$8{\cdot}56 \times 10^{-3}$	$2{\cdot}89 \times 10^{-3}$

[a] *Ca.* $4{\cdot}5 \times 10^{-4}$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_ψ) in the usual way, and for splitting the k_ψ values into rate coefficients for the constituent reactions, k_d for decomposition to nitrobenzene and k_p for conversion into the "protected" form, (**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 (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 Virtanen[5] have shown by a stopped-flow kinetic study that (**1**) and NaOMe react very rapidly (k $3{\cdot}0 \times 10^8$ M^{-1} 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 [$\Delta H^{\ddagger}$ 15 kcal mol^{-1} and $\Delta S^{\ddagger}$ -14 cal deg^{-1} mol^{-1} for (**3**) $\rightarrow$ (**2**), $\Delta H^{\ddagger}$ 19 kcal mol^{-1} and $\Delta S^{\ddagger}$ -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 25M-iodobenzene forms nitrobenzene and 1-iodo-4 nitrobenzene in approximately equal amounts indicates a radical mechanism[7] and thus that a non-radical, intramolecular transformation[4] is at most a minor reaction pathway

This research was supported in part by the American Chemical Society Petroleum Research Fund W J B , jun , acknowledges a National Science Foundation Postdoctoral Fellowship

(*Received, August 13th*, 1971, *Com* 1409)

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[1] J F Bunnett and H Takayama, *J Org Chem* , 1968, **33**, 1924

[2] H v Pechmann and L Frobenius, *Ber* , 1894, **27**, 672

[3] H Hoch, personal communication

[4] *Cf* also A Hantzsch, *Ber* , 1894, **27**, 2968

[5] C D Ritchie and P O I Virtanen, *J Amer Chem Soc* , in the press

[6] J F Bunnett and H Takayama, *J Amer Chem Soc* , 1968, **90**, 5173

[7] J F Bunnett and C C Wamser, *J Amer Chem Soc* , 1966, **88**, 5534, D L Brydon and J I G Cadogan, *J. Chem Soc.* (*C*), 1968, 819