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REACTION BETWEEN NITROAROMATIC COMPOUNDS AND NITRITE ION IN APROTIC POLAR SOLVENTS

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In hexamethylphophoramide, ^{18}O-labelled nitrite ion readily exchanged with the nitro group of p-dinitrobenzene at 30°C, whereas the formation of p-nitrophenol by the O-attack of nitrite ion is much slower. p-Nitrochlorobenzene is quickly converted to p-dinitrobenzene by the N-attack of nitrite ion, and p-nitrophenol is the final product. The nitro group of p-nitrobenzonitrile is slowly exchanged with nitrite ion.

Recently Broxton, Muir, and Parker reported the results of their ^{15}N study on the reactions between nitrohalobenzenes and nitrite ion in hexamethylphosphoramide (HMPA).[1] We have been investigating the reactions between nitroaromatic compounds and nitrite ion by using oxygen-18, and we wish to report the results of our study.

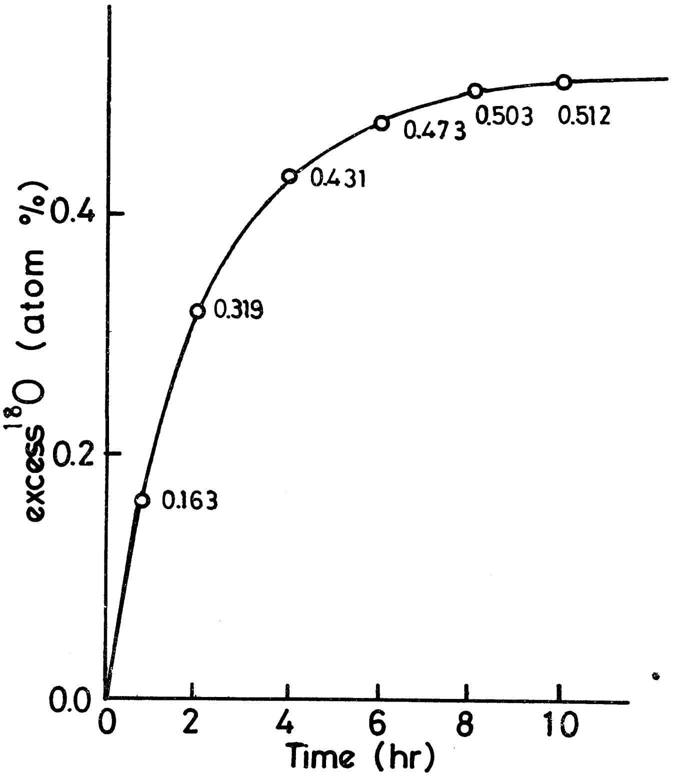
Nitrite ion is an ambident ion. It is known that upon reaction with aliphatic halides it gives both nitrite esters (O-attack) and nitro compounds (N-attack), and their relative yields vary with the structure of halides and the reaction conditions.[2] It is also known that anions show greater nucleophilicity in aprotic polar solvents than in protic solvents. However, the nucleophilic reactions of nitrite ion in aprotic polar solvents have not been reported in the literature, and therefore we started our study on the reactions between nitrite ion and nitrohalobenzenes in DMSO, HMPA, and DMF.

It was found that nitrite ion readily reacts with p-nitrochlorobenzene and p-nitrobromobenzene, yielding p-nitrophenol and 4,4'-dinitrodiphenyl ether in both cases. When ^{18}O-labelled nitrite ion was used, the 4,4'-dinitrodiphenyl ether obtained was found to possess excess oxygen-18 at not only the ether oxygen atoms but also the nitro oxygen atoms. Since such facile exchange between nitrite ion and the nitro groups on nitrobenzenes has not been described in the literature, we carried out a study on the reactions between ^{18}O-labelled nitrite ion (excess ^{18}O, 1.008 atom %)and various substituted nitrobenzenes in HMPA.

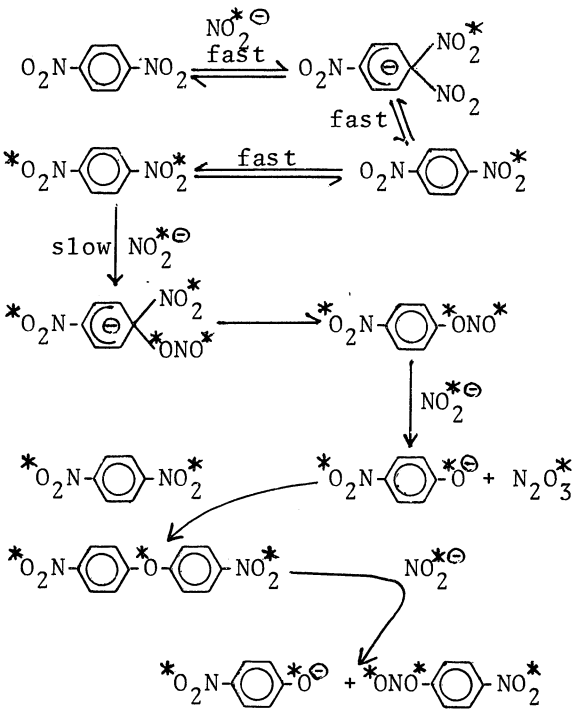
The nitro groups of p-dinitrobenzene readily exchanged with ^{18}O-labelled nitrite ion in HMPA at 30°C, and the ^{18}O content reached an equilibrium value in about 8 hr. Fig. 1 shows the change of the ^{18}O excess content in the recovered p-dinitrobenzene with time. The rate constant for the exchange was calculated from a second order equation; $k_{30°C} = 2.8 \times 10^{-3}\ M^{-1}sec^{-1}$.

The formation of p-nitrophenol was fairly rapid at 70°C, but very slow at 34°C;

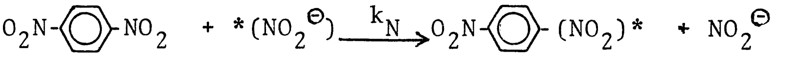
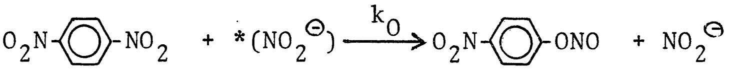
Fig. 1. Change of the ^{18}O Content in the p-Dinitrobenzene Recovered



$k_{34°C}$ = 8.7 x 10^{-5} $M^{-1}sec^{-1}$ (determined from the decrease of $C_6H_4(NO_2)_2$ and increase in $^{\ominus}OC_6H_4NO_2^{\,-}$ in the NMR spectra). The reactions taking place are represented by the scheme shown below.

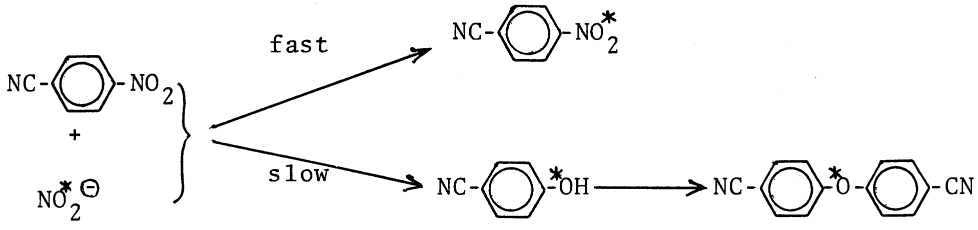


Broxton, Muir, and Parker indirectly calculated the rate constant for the displacement of the nitro group of p-dinitrobenzene with ^{15}N-labelled nitrite ion; they determined the rate of production of $^{\ominus}OC_6H_4NO_2$ spectrophotometrically, determined the ^{14}N, ^{15}N proportions in p-nitrophenol by mass spectrometry, and then calculated the rate constant for the N-attack from these data.

	This work	Broxton, et al.
	2.8 x 10^{-3} (30°,HMPA)	6.4 x 10^{-4} $M^{-1}sec^{-1}$ (100°C,DMSO)
	8.7 x 10^{-4} (34°, HMPA)	2.7 x $10^{-4}M^{-1}sec^{-1}$ (100°C, DMSO)

They also reported that the k_N/k_O in HMPA at 100°C is 2. Our rate constants and their rate constants differ much; 1) our k_N at 30°C in HMPA is much greater than their k_N at 100°C in DMSO, 2) our k_N/k_O is much greater than their k_N/k_O ratio. The discrepancy must be solved by further investigation.

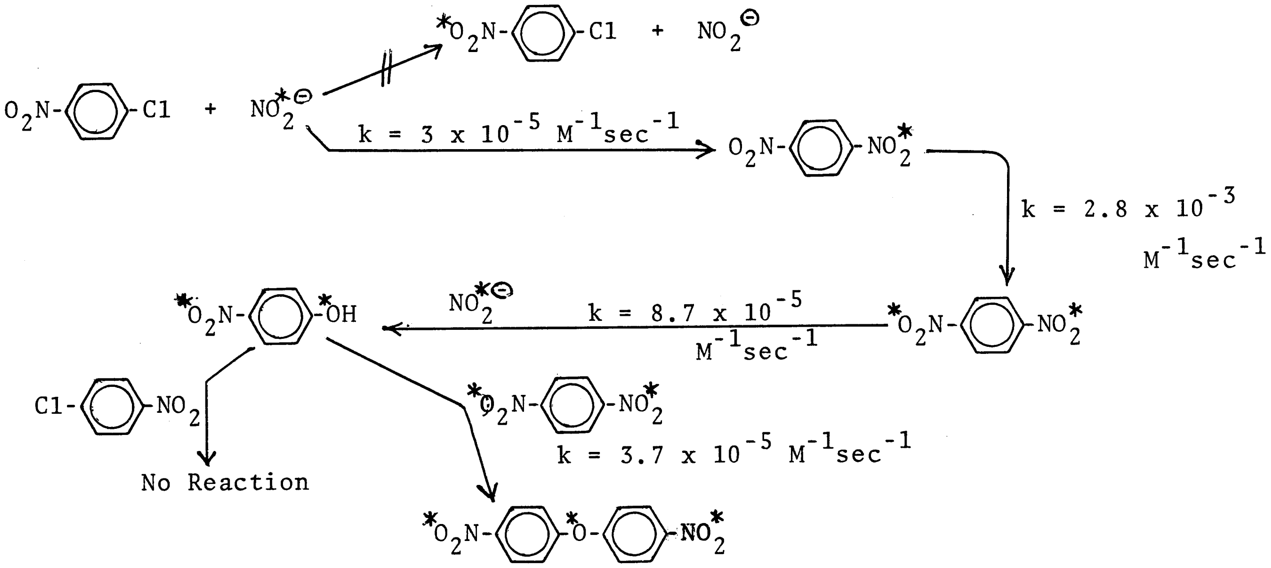
When p-nitrobenzonitrile and ^{18}O-labelled sodium nitrite were allowed to react in HMPA at 60°C, the ^{18}O analysis of the recovered p-nitrobenzonitrile showed that the ^{18}O-incorporation to p-nitrobenzonitrile took place slowly at 60°C (0.10% excess ^{18}O after 20 hr), but the products of O-attack were not observable by NMR. When the reaction was carried out at 100°C, p-cyanophenol and 4,4'-dicyanodiphenyl ether were found as products. These results suggest that the reactions taking place are similar to those observed for p-dinitrobenzene, that is, faster N-attack and slower O-attack of nitrite ion to the nitro group of p-nitrobenzonitrile.



When p-nitrochlorobenzene and ^{18}O-labelled sodium nitrite were allowed to react in HMPA at 34°C, the recovered p-nitrochlorobenzene contained no excess ^{18}O atoms. It was found that p-nitrochlorobenzene was slowly converted to p-dinitrobenzene ($k_{34°C} = 3 \times 10^{-5}\ M^{-1}sec^{-1}$; the p-dinitrobenzene formed is slowly further converted to p-nitrophenol by the O-attack of nitrite ion, and hence this rate constant is not so acccurate).

The formation of p-nitrophenol can be ascribed to either the displacement of Cl in p-nitrochlorobenzene by $^{\ominus}$ONO or the displacement of NO_2 in p-dinitrobenzene by ONO$^{\ominus}$. However, since both the hydroxy and nitro oxygens of the p-nitrophenol obtained were found to contain excess ^{18}O atoms, the main path for the formation of p-nitrophenol must be that involving p-dinitrobenzene as the intermediate.

The formation of 4,4'-dinitrodiphenyl ether can be ascribed to the attack of p-nitrophenoxide anion to either p-nitrochlorobenzene or p-dinitrobenzene. However, separate experiments showed that the reaction between p-nitrophenoxide anion and p-chloronitrobenzene is much slower (34°C, no reaction; 100°C, $k = 5.4 \times 10^{-5}\ M^{-1}sec^{-1}$) than that between p-nitrophenoxide anion and p-dinitrobenzene (34°C, $k = 3.7 \times 10^{-5} M^{-1}sec^{-1}$). Therefore, the reactions taking place at 34°C can be represented as follows.



REFERENCES

1. T. J. Broxton, D. M. Muir, and A. J. Parker, J. Org. Chem., 40, 2037 (1975).
2. N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, J. Amer. Chem. Soc., 77, 6269 (1955).
N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, J. Amer. Chem. Soc., 78, 1497 (1956).

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