NITROSATION OF *N,N*-DIMETHYLANILINE AND NITRATION OF BENZENE IN MOLTEN SALTS

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Abstract

The nitration of reactive aromatic compounds in molten nitrate–pyrosulphate mixtures has previously been offered as evidence in support of the existence of NO_2^+ in the melt. An examination of the nitrosation of *N,N*-dimethylaniline in molten (K,Na)NO_2 and a re-examination of the nitration of benzene using molten nitrates indicated that these reactions were occurring in the vapour phase above the melt. Consequently such experiments can no longer be offered in support of the existence of NO_2^+ in molten salts.

Introduction

Temple, Fay, and Williamson[1] nitrated a number of organic compounds by passing their vapour through a solution of pyrosulphate in molten nitrate. They put forward their results as support for the hypothesis of Duke and coworkers,[2,3] that nitrate ion is dissociated in the melt to form oxide ion and nitryl ion

$$NO_3^- \rightleftharpoons NO_2^+ + O^{2-}$$

although previous attempts to identify NO_2^+ in molten nitrates directly had failed.[4,5]

Following this we attempted to extend the work to molten nitrites to see if evidence for NO^+ could also be obtained chemically. For a molten nitrite a similar self-dissociation equilibrium could be proposed:

$$NO_2^- \rightleftharpoons NO^+ + O^{2-}$$

The nitrosyl ion (NO^+) is thought to be the agent responsible for nitrating certain organic compounds such as *N,N*-dimethylaniline in dilute nitric acid, where an intermediate nitroso compound is formed. We studied what took place when *N,N*-dimethylaniline vapour was passed through molten (K,Na)NO_2 containing $S_2O_7^{2-}$ at 310°C. In the light of our results, we subsequently re-examined the nitration of benzene as previously reported by Temple, Fay, and Williamson.

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[1] Temple, R. B., Fay, C., and Williamson, J., *Chem. Commun.*, 1967, 966.

[2] Duke, F. R., and Iverson, M. L., *J. Am. chem. Soc.*, 1958, **80**, 5061.

[3] Duke, F. R., and Yamamoto, S., *J. Am. chem. Soc.*, 1959, **81**, 6378.

[4] Topol, L. E., Osteryoung, R. A., and Christie, J. H., *J. phys. Chem.*, 1966, **70**, 2857.

[5] Inman, D., and Braunstein, J., *Chem. Commun.*, 1966, 148.

Experimental

The experimental apparatus was similar to that previously described.[1] $K_2S_2O_7$ was added from time to time in tablet form, as its reaction with the nitrite melt is very vigorous and complete. The material recovered from the receivers consisted largely of unchanged starting material but by shaking the product with ether and water (pH 6) it was possible to separate the reaction products from the large amount of unchanged dimethylaniline. The aqueous phase was made alkaline to pH 11 with solid Na_2CO_3 and extracted with chloroform, which was subsequently dried and evaporated. A small quantity of bright green product was obtained and was finally identified by mass, infrared, and n.m.r. spectroscopy as *p*-nitroso-*N*,*N*-dimethylaniline. The percentage yield (based on dimethylaniline passed in) was determined gravimetrically. In several cases the product also contained small amounts of aliphatic secondary amines and/or nitrosocondensation products (possibly "azoxy" compounds[6]). Unless the dimethylaniline was vigorously purified before use by boiling with acetic anhydride, the presence of impurities such as aliphatic amines or secondary aromatic amines resulted in the formation of small quantities of intensely blue substances which were identified as "Wurster's Blue" derivatives. These are radical ions, structurally analogous to semiquinones[7] and are frequently dimeric. They may be prepared[8] by treating tetramethylphenylenediamine with NO in the presence of H_2SO_4 and ethanol. In this work the presence of nitrogen oxides and $K_2S_2O_7$ results in comparable conditions.

The procedures for the nitration of benzene were essentially the same as those of the nitrosation reaction, except that the reaction products consisted only of benzene and nitrobenzene, with a small amount of strongly acid water. The products were extracted in ether and the aqueous phase separated. The ether phase was dried and the excess ether evaporated. The benzene fraction was removed by distillation in a micro Quick-fit apparatus and the pure nitrobenzene weighed. This procedure was checked using several standard mixtures of benzene and nitrobenzene and cross-checks were performed by measuring refractive indices and by using gas–liquid chromatographic procedures.

Results and Observations

Without the addition of potassium pyrosulphate, no nitrosation products were obtained when *N*,*N*-dimethylaniline was passed through the melt. Using an arbitrary set of addition rates of $K_2S_2O_7$ (4·0 g) and dimethylaniline (7·5 ml over 15 min) to the $(K/Na)NO_2$ eutectic (210 ± 1 g) at 310°C, it was found that the highest percentage yield obtained was *c.* 3·5% based on the dimethylaniline passed in. The yield was variable and found to decrease as the melt temperature was increased.

When the same melt was used continually the yields obtained in successive experiments were seen to fall gradually. It was suspected that this was connected with the gradual removal of water from the melt. When water vapour was deliberately introduced with the dimethylaniline vapour into such a melt, the yield of nitroso compound rose from *c.* 0·5% to the original figure.

Further experiments showed that comparable yields of nitroso compound were also obtained if the dimethylaniline vapour was introduced into the gas stream just after it has left the melt. It thus appeared that the nitrosation is not a true melt reaction but that it can take place in the vapour phase above the melt.

On re-examination of the nitration of benzene by pyrosulphate solutions in molten nitrate, we found that this reaction can also occur in the vapour phase over the melt and is thus probably not a true melt reaction either.

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[7] Friend, J. A., and Roberts, N. K., *Aust. J. Chem.*, 1958, **11**, 104.
[8] Willstätter, R., and Piccard, J., *Ber. dt. chem. Ges.*, 1908, **41**, 1458.

Experiments in which the mole percentage of $LiNO_3$ in the $(K/Li)NO_3$ melt was varied showed that the yield of nitrobenzene obtained appeared to rise linearly with Li content up to *c.* 30 mole per cent in the melt and afterwards levelled off (*c.* 12% yield of nitrobenzene). In those melts which were not adequately dried by pre-evacuation, the yield of nitrobenzene was greater than that normally obtained (i.e. >12% based on benzene passed in).

In each case the nitrating or nitrosating agent must be produced in the melt and persist long enough to bring about the gaseous reaction. Topol *et al.*[4] were unable to identify NO_2^+ in molten nitrates polarographically, and suggested that all reactions attributed to it can be explained as reactions of NO_2. However, Williamson[9] showed that NO_2 vapour will not nitrate benzene vapour if the two are passed together through molten nitrate by itself at 300°C. This fact, and our observation that water is essential for the reaction, lead us to believe that the agents responsible for nitration and nitrosation are probably the gaseous molecules HNO_3 and HNO_2 respectively. Although unstable, these molecules may persist long enough to bring about the reactions as observed. They may possibly be produced in the following reactions

$$2NO_3^- + S_2O_7^{2-} \rightleftharpoons 2SO_4^{2-} + N_2O_5(g) \quad (A)$$

$$N_2O_5(g) + H_2O(g) \rightleftharpoons 2HNO_3(g) \quad (B)$$

and

$$2NO_2^- + S_2O_7^{2-} \rightleftharpoons 2SO_4^{2-} + N_2O_3(g) \quad (C)$$

$$N_2O_3(g) + H_2O(g) \rightleftharpoons 2HNO_2(g) \quad (D)$$

In support of the latter scheme it should be noted that the trap cooled in liquid nitrogen does contain noticeable amounts of a bright blue compound that disappears rapidly on warming to room temperature, and which is most probably N_2O_3. Reaction (A) has been proposed originally by Duke and Yamamoto[3] while (C) receives support from the work of Topol *et al.*[4]

As the reaction appears to take place in the vapour (and perhaps in the gaseous emulsion produced by the reaction of $K_2S_2O_7$ with the melt), nitration experiments can no longer be offered in support of the existence of NO_2^+ and NO^+ in these melts. Recently, Zambonin[10] has shown that even under considerable water pressures (e.g. 10 Torr) or in "perfectly dry and nitrite free melts", the equilibrium concentrations of NO_2^+ are approximately the same. Thus the increasing yield of nitrobenzene with increasing water content of the melt cannot be explained in terms of an increased concentration of $H_2NO_3^+$ in the melt.[11]

[9] Williamson, J., M.Sc. Thesis, University of Sydney, 1968.
[10] Zambonin, P. G., *J. electroanal. Chem.*, 1971, **32**, App. (1–4).
[11] Bartholomew, R. F., and Garfinkel, H. M., *J. inorg. nucl. Chem.*, 1969, **31**, 3655.