Molten Salts as Reaction Media: the Nitration of Organic Compounds in Molten Nitrates

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MANY molten salts and their mixtures have physical properties that suggest their possible use as reaction media for both inorganic and organic reactions, though little use has so far been made of them. This is surprising, since the results obtained[1] have both fundamental and practical interest. Our results were obtained during a study of molten nitrate mixtures as media for organic reactions.

The nitrate ion has a tendency to dissociate into nitronium and oxide ions,

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

but under normal conditions the equilibrium concentration of NO_2^+ is very small indeed. It can be increased by adding certain ions which combine with O^{2-}, for example by adding $S_2O_7^{2-}$, and the equilibrium constant for the overall reaction

$$NO_3^- + S_2O_7^{2-} \rightleftharpoons 2SO_4^{2-} + NO_2^+$$

is very much larger than that for the dissociation of the nitrate ion alone.[2] Since NO_2^+ is known to be the agent responsible for the nitration of organic substances when nitric acid is used,[3] it seemed probable that nitrate melts containing $S_2O_7^{2-}$ would also be capable of promoting organic nitrations. We have now shown that this is true for several organic substances.[4]

To reduce experimental difficulties and allow the greatest variation in reaction temperature, we have used a eutectic mixture of lithium, potassium, and sodium nitrates (mole ratios of Li : Na : K = 30 : 16 : 54) which melts at 120°. This melt can be handled in Pyrex apparatus and is dehydrated simply by pumping off the water vapour at a temperature just above the melting point. A stream of dry oxygen-free nitrogen was used as a carrier gas, the flow-rate being monitored with a ball-and-tube flowmeter. The organic material was introduced into the nitrogen as vapour, and the combined vapours were then passed through the melt, which was heated electrically to a suitable temperature. The vapour from the reaction vessel was cooled in two traps in series, the first immersed in ice, the second in liquid nitrogen. The condensate was dried (Na_2SO_4), and samples were then injected into a Shimadzu Model GC-1C gas–liquid chromatograph.

Twelve different starting materials were tried and nitration products were identified in all but three cases. These results are summarized in the Table.

Although no effort was made in these experiments to improve the yield of product, it is interesting to quote the percentage yield obtained in the nitration of benzene by way of example. Using a melt consisting initially of 100 g. of nitrate mixture to which 5 g. of potassium pyrosulphate had been added, 19 ml. of benzene were vaporized and passed into the melt. 13 ml. of product were condensed in the traps, and 1·4 ml. was recovered from the melt. G.l.c. analysis, using helium as the carrier gas, showed that the product contained 70% nitrobenzene and 30% unchanged benzene with no indication of the presence of di- or tri-nitrobenzenes. The yield of nitrobenzene was therefore approximately 60% of the theoretical, calculated on the amount of benzene consumed. This is remarkably high, especially since the time of contact between the vapour and the melt had been very short, *i.e.*, less than 2 seconds in all the experiments reported here. This short contact-time may possibly explain our failure to nitrate methane in the one experiment tried. On the other hand it seems probable that the failure is due to the existence of a different nitrating mechanism for aliphatic compounds, one not involving NO_2^+.

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TABLE

Products obtained from various organic materials using nitrate melt containing $S_7O_2^{2-}$

Reactant	Temperature	Products(s)	Remarks
Benzene	250°	Nitrobenzene	No di- or tri-nitrobenzene detected on chromatogram.
Nitrobenzene	300°	*m*-Dinitrobenzene	No tri-nitrobenzene detected.
Toluene	250°	Mononitrotoluenes	54% *o*- 42% *p*- 4% *m*-
Chlorobenzene	250°	Mononitrochlorotoluenes	35% *o*- 63% *p*- 2% *m*-
Bromobenzene	250°	Mononitrobromotoluenes	30% *o*- 65% *p*- 2% *m*-
Benzoic acid	350°	*m*-Nitrobenzoic acid	No *ortho*- or *para*-isomer detected.
Aniline	250°	—	Oxidation products only.
Pyridine	300°	3-Nitropyridine	No 2- or 4-nitroisomer.
Naphthalene	300°	1-Nitronaphthalene	Naphthalene ignited!
Benzaldehyde	300°	—	Oxidation products only.
Methane	250°	—	No reaction.
Hexane	250°	1-Nitrohexane	Hexane ignited.

[1] W. Sundermeyer, *Angew. Chem. Internat. Edn.*, 1965, **4**, 222.

[2] F. R. Duke and S. Yamamoto, *J. Amer. Chem. Soc.*, 1959, **81**, 6378.

[3] C. Ingold, "Structure and Mechanism in Organic Chemistry", Bell, London, 1953.

[4] R. B. Temple and C. Fay, provisional Australian Patent Application No. 20640/67.