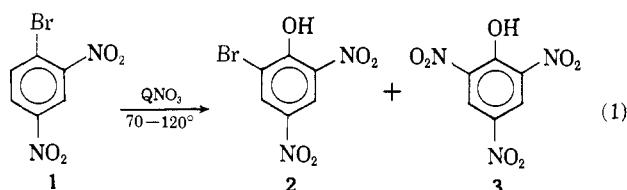


Fused Organic Salts. I. Bromohydroxy- and Nitrohydroxydebromination and Other Reactions of Organic Halides with Molten Quaternary Ammonium Nitrates

Sir:

The chemical and physical properties of molten organic salts have received little attention,¹ presumably due to the usual narrowness or nonexistence of a working temperature range between the freezing point and the stability limit. Many low-melting salts have, however, been reported. In the present work on a collection of these with $50^\circ < \text{f.p.} < 120^\circ$, solid-liquid phase diagrams for a large number of salt-salt and salt-organic nonelectrolyte systems have been studied.² These show complete liquid-liquid miscibility to be the general rule for systems of molten tetra-*n*-alkylammonium salts in the pentyl-heptyl range with most organic nonelectrolytes except saturated hydrocarbons. This suggests use of these melts as interesting media for organic reactions. Since both ion association^{1g,h} and anion solvation are absent in such melts, one might expect nucleophilic anions to display enhanced reactivities in these media, which can be regarded as the ultimate stage in the progression of media: protic solvent, dipolar aprotic solvent, fused salt.³

tetra-*n*-hexylammonium nitrate (hereafter Q(6)NO₃), in 3 hr. at 82°, to products derived from 2,4-dinitrophenol. The transformation observed is



The reaction can be made to give either product in high yield. (a) Heating⁵ a mixture of 1 (1.00 mmole) and tetra-*n*-pentylammonium nitrate, Q(5)NO₃, (1.20 mmoles, m.p. 112.5–113.5°) at 107–125° for 3 hr. gave a red oil which was chromatographed on silicic acid (12 g.). The benzene-eluted phenol mixture was dissolved in methylene chloride and extracted with aqueous buffers of pH 4.3 and 8.0 from which picric acid (0.865 mmole, 86%, m.p. 120–121.5°) and 2 (0.06 mmole, 6%), melting point and infrared spectra identical with those of authentic materials, were obtained by acidification and extraction. (b) Q(5)NO₃ (1.39 mmoles), Q(5)Br (1.39 mmoles, m.p. 101°), and 1 (1.39 mmoles), fused for 1.1 hr. at 103–115° and simi-

TABLE I
REACTIONS OF 2,4-DINITROPHENYL DERIVATIVES WITH FUSED QNO₃ AND QNO₂

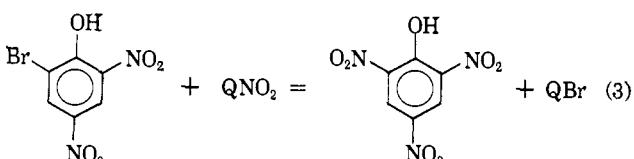
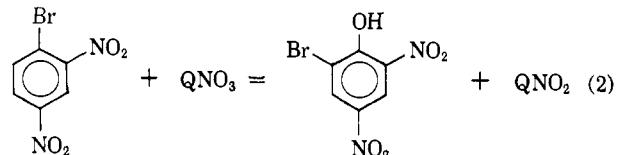
Expt.	Reactants ^a	Salt	Conditions		Products, %				Anal. Method
			Temp., °C.	Time, min.	X	OH	O ₂ N	OH	
1	X = Br	Q(5)NO ₃	107	5	33	67			N.m.r.
2	Br	Q(5)NO ₃	107	13	21	66	13		N.m.r.
3	Br	Q(5)NO ₃	107	120	7	16	77		N.m.r.
4	I	Q(5)NO ₃	105–120	120	?	41	38		Isol.
					16	48	36		N.m.r.
5	Cl	Q(5)NO ₃	100–115	240	22	31	10	22	Isol.
6	OTs	Q(5)NO ₃	107–110 (1.1)	120	13		61	19	Isol.
7	2	Q(5)NO ₃ (1.2)	107–120	120		14	80		Isol.
8	X = OH	Q(5)NO ₃ Q(5)Br	100–120	60		78		22	N.m.r.

^a Mole ratio of salt to substrate 1.0 unless otherwise given in parentheses.

New reactions of fused quaternary ammonium nitrates, QNO₃, have now been found in which nitrate ion, a very poor nucleophile in most media,⁴ is indeed a highly reactive agent. Thus, although 2,4-dinitrobromobenzene, 1, is inert toward silver nitrate or QNO₃ in refluxing acetonitrile, it is 83% converted by molten

larly worked up, gave 2 (1.31 mmoles, 94%, m.p. 116–117.5°) and 3 (0.03 mmole, 2%). Further experiments are summarized in Table I.

The reaction proceeds in two stages (expt. 1–3); these have been identified as



(1) The literature is rapidly summarized: (a) T. D. Stewart and J. G. Aston, *J. Am. Chem. Soc.*, **48**, 1642 (1926); **49**, 1718 (1927); thermal analysis, conductance (C). (b) P. Walden, *et al.*, *Z. physik. Chem.*, **160**, 57 (1932) and earlier papers: melt densities (D), viscosities (V), C. (c) L. F. Audrieth, *et al.*, *J. Am. Chem. Soc.*, **58**, 428 (1936), and earlier papers: solutions of metal salts, electrodeposition (ED). (d) F. H. Hurley and T. P. Wier, Jr., *J. Electrochem. Soc.*, **98**, 203 (1951); ED. (e) R. P. Seward, *J. Am. Chem. Soc.*, **73**, 515 (1951); D, V, C. (f) P. L. Mercier and C. A. Kraus, *Proc. Natl. Acad. Sci. U. S.*, **42**, 65, 487 (1956); phase relations, C, V. (g) R. P. Seward, *J. Phys. Chem.*, **66**, 1125 (1962); cryoscopy. (h) L. C. Kenausis, E. C. Evers, and C. A. Kraus, *Proc. Natl. Acad. Sci. U. S.*, **48**, 121 (1962); **49**, 141 (1963); D, V, C. (i) M. Goffman and G. W. Harrington, *J. Phys. Chem.*, **67**, 1877 (1963); molten pyridinium chloride and bischloride. (j) T. R. Griffiths, *J. Chem. Eng. Data*, **8**, 568 (1963); D. Hydrated salts are not considered.

(2) J. E. Gordon, to be published.

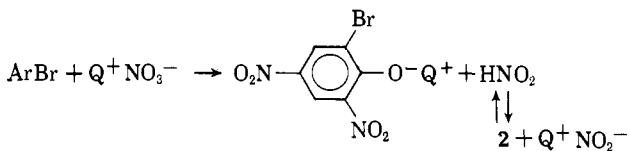
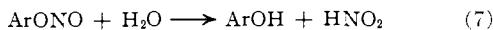
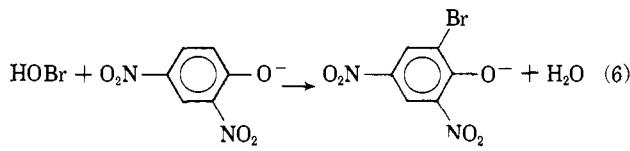
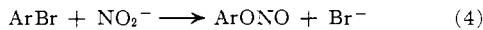
(3) J. F. Bennett, *Annu. Rev. Phys. Chem.*, **14**, 281 (1963).

(4) W. L. Petty and P. L. Nichols, Jr., *J. Am. Chem. Soc.*, **76**, 4385 (1954).

(5) These are smooth, nonexplosive reactions. Nevertheless, heating such mixtures is potentially hazardous and all reactions were carried out in a hood behind a safety shield.

Reaction 3 is analogous to the nitrodebromination of bromophenols known⁶ to be effected by nitrous acid in acetic acid. This QNO_2 -2 reaction was independently demonstrated (expt. 7). Kinetic data for reaction 2 (1 with $\text{Q}(6)\text{NO}_3$ at 75°), when plotted as a second order NO_3^- -1 reaction, produced the S-shaped curve characteristic of an autocatalytic process. Addition of 10 mole % of QNO_2 increased the initial rate ~75-fold, implicating NO_2^- as the autocatalyst. In view of the superior nucleophilicity of NO_2^- , the catalysis can be identified with the initial displacement of bromide, $\text{ArBr} + \text{NO}_2^- \rightarrow \text{ArONO} + \text{Br}^-$. An elevated oxidation state of bromine must then be sought to account for bromination of the 2,4-dinitrophenol nucleus thus generated.

This was found in the surprising power of nitrate ion to oxidize bromide in the presence of weak acid in the molten salt medium (expt. 8).⁷ This reaction does not occur detectably in water or acetonitrile. In the QBr - QNO_3 - ArOH melt it is also possible to trap bromine as stilbene dibromide. Reaction 2 can reasonably be accounted for as the sum of (4)-(7) ($\text{Ar} = 2,4$ -dinitrophenyl).



9-Bromofluorene (1.00 mmole) fused with $\text{Q}(5)\text{NO}_3$ (1.00 mmole) for 0.25 hr. at 105° and chromatographed on 11 g. of silicic acid gave 9-fluorenone (0.53 mmole) and 9-fluorenol (0.13 mmole) as benzene-eluted fractions. Similarly treated, *p*-nitrobenzyl bromide produced *p*-nitrobenzaldehyde (15%), *p*-nitrobenzoic acid (6%), and *p*-nitrobenzyl *p*-nitrobenzoate (26%). Molten $\text{Q}(5)\text{NO}_3$ converted 2-bromopropane principally to propene (32%), 2-propanol (24%), and acetone (9%), with smaller amounts of 2-propyl nitrate and nitrite, 2-propyl ether, and 2-nitropropane.⁸

It appears that molten QNO_3 , though indeed reactive, owes its reactivity not to enhanced NO_3^- nucleophilicity but to facile oxidation-reduction processes in the melt.

Further details of these reactions will be reported together with results on other systems.

(6) T. Zincke, *J. prakt. Chem.*, [2] **61**, 561 (1900).

(7) This reaction is both thermodynamically unfavorable and very slow in water; only in rather concentrated nitric acid is it observed.

(8) Sealed tube at 120-125° for 3 hr., analysis by gas chromatography; identification by retention time, confirmed by infrared and n.m.r. spectra of the product mixture.

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The Rates of Pyridinyl Radical Reactions

Sir:

We report here the measurement of the rates of halogen abstraction by 1-ethyl-4-carbomethoxypyridinyl (1), a stable free radical,¹ and the conclusion that the reaction is atom transfer. This is the first report of the direct measurement of such a reaction, and the data allow straightforward conclusions about the transition states of the reactions.^{2a}

Radical 1 was prepared by zinc metal reduction of the pyridinium iodide and isolated by distillation.¹ Solutions of 1 were treated with a large excess of dibromomethane (2), bromochloromethane (3), or dichloromethane (4) (a special apparatus permitted observation of spectral changes *in situ*). The rates were followed by means of the visible absorption band of 1. The rate of disappearance of 1 was cleanly first order in all cases. The second-order constants were obtained by dividing by the concentration of halocarbon. The results are tabulated in Table I.

TABLE I
RATES OF PYRIDINYL RADICAL REACTIONS

Radical concn., $\times 10^{-2} \text{ M}$	Halocarbon concn. (M)	Temp., ^f °C.	$k_{\text{obsd.}}$ sec. ⁻¹	$k_2,^a$ 1. mole ⁻¹ sec. ⁻¹
1.20	CH_2Br_2 (0.84)	CH ₃ CN 25	3.43×10^{-4}	2.0×10^{-4b}
1.12	CH_2Br_2 (1.30)	CH ₃ CN 25	5.33×10^{-4}	2.1×10^{-4b}
0.54	CH_2Br_2 (0.41)	CH ₃ CN 25	1.52×10^{-4}	1.9×10^{-4b}
0.88	CH_2Br_2 (0.84)	CH ₂ Cl ₂ 25	1.60×10^{-4}	1.0×10^{-4b}
1.74	CH_2Br_2 (0.84)	<i>i</i> -PrOH 25	0.94×10^{-4c}	0.6×10^{-4b}
0.22	CH_2Br_2 (1.28)	EtOH 25	$\sim 1.7 \times 10^{-4d}$	$\sim 0.7 \times 10^{-4b}$
1.13	CH_2BrCl (0.84)	CH ₃ CN 25	8.57×10^{-5}	1.0×10^{-4}
0.83	CH_2Cl_2 (0.85)	CH ₃ CN 75	8.68×10^{-6}	5.1×10^{-6b}
0.59	CH_2Cl_2 (0.85)	CH ₃ CN 50	1.06×10^{-6}	6.2×10^{-7b}
e	CH_2Cl_2 (0.85)	CH ₃ CN 25	9.10×10^{-5}	5.4×10^{-8b}

^a Estimated reliability 5-7%. ^b Corrected by dividing the measured k_2 by the statistical factor of 2. ^c Corrected for the solvent reaction with radical, with $k_1 = 2.61 \times 10^{-5}$ sec.⁻¹ for 0.84 M CH_2Cl_2 in isopropyl alcohol ($Z = 75.5$). A solution 0.84 M CH_2Br_2 in isopropyl alcohol has $Z = 75.8$. ^d Estimated after an approximate correction for the reaction of solvent with radical. ^e Extrapolated from the data at higher temperatures using $E_a = 19$ kcal./mole. ^f Radical solutions in acetonitrile decrease in concentration at 75° with a half-life of 12 days.

The reaction of radical 1 with halocarbons produces 50% 1-ethyl-4-carbomethoxypyridinium halide [λ_{max} 2740 and 2200 Å., lit.^{2b} λ_{max} 2735 and 2200 Å. (ϵ 4500 and 12,000), yield $51 \pm 4\%$ in seven experiments, measured by quantitative ultraviolet spectroscopy in water at 2740 Å., silver halide formation with silver ion] and reduced pyridine derivatives [soluble in hexane, volatile, sensitive to oxygen (from 2), λ_{max} 2420 Å. ($\epsilon \sim 10,000$), reported for 1,4,4-trimethyl-1,4-dihydropyridine λ_{max} 2708 and 2305 Å. (ϵ 3200 and 7500),³ along with small amounts of polymeric material. Equation 1 summarizes these results for the reaction of 1 with 2 and includes two reasonable structures for the dihydropyridines.

The rate of the reaction of radical 1 with 2 is changed very little with a variation in solvent polarity over a wide range, from dichloromethane ($Z = 64.2^4$) through

(1) E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.*, **85**, 2035 (1963).

(2) (a) The disproportionation of moderately stable phenoxyl radicals has been reported by C. D. Cook and B. W. Norcross, *ibid.*, **81**, 1176 (1959); (b) E. M. Kosower, "Molecular Biochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 185.

(3) E. M. Kosower and T. S. Sorensen, *J. Org. Chem.*, **27**, 3764 (1962).