

Fused Organic Salts. II.¹ Reactions of Organic Halides with Molten Quaternary Ammonium Nitrates

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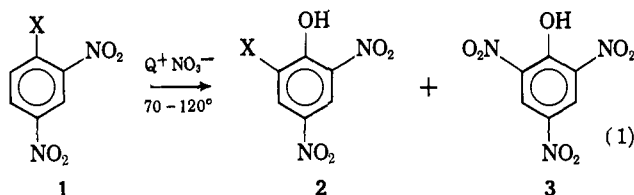
2,4-Dinitrobromobenzene reacts with molten quaternary ammonium nitrates, $Q^+NO_3^-$, at 75–125° to give 2-bromo-4,6-dinitrophenol (2) and picric acid (3). The reaction proceeds in two stages, producing first 2 + $Q^+NO_2^-$ which are then transformed into 3 + Q^+Br^- . Suitable modifications allow either product to be isolated in high yield. 2,4-Dinitrochloro- and 2,4-dinitroiodobenzene react similarly but less completely. $Q^+NO_3^-$ converts the corresponding tosylate to 3. Study of the reaction kinetics, of the effect of additives, and of side reaction products and potential intermediates indicates a catalytic oxidation–reduction mechanism in which the first stage proceeds by displacement of Br^- by NO_2^- , oxidation of Br^- by NO_3^- , and bromination of 2,4-dinitrophenol. Fluorenyl bromide with $Q^+NO_3^-$ gives fluorenone (53%) and fluorenone (13%). *p*-Nitrobenzyl bromide gives *p*-nitrobenzyl alcohol (12%), *p*-nitrobenzaldehyde (15%), *p*-nitrobenzoic acid (6%), and *p*-nitrobenzyl *p*-nitrobenzoate (26%). 2-Bromopropane and $Q^+NO_3^-$ produce a variety of products among which propene, 2-propanol, and acetone predominate.

Introduction

As part of a general study of chemical and physical properties of fused organic salts, the possibility that anions in such melts might possess enhanced nucleophilic character was of interest. In one sense, the fused salt is the logical extremity of the series of media²: protic solvent, dipolar aprotic solvent, and fused salt. New reactions of molten quaternary ammonium nitrates have now been discovered in which the very poorly nucleophilic nitrate ion displays an apparent high order of reactivity.³ This report describes these reactions and attempts to elucidate the nature of this reactivity.

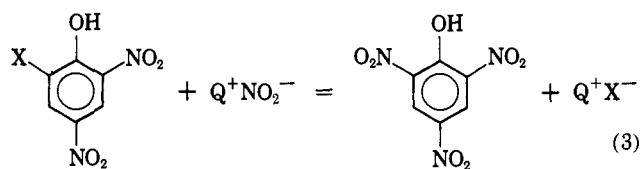
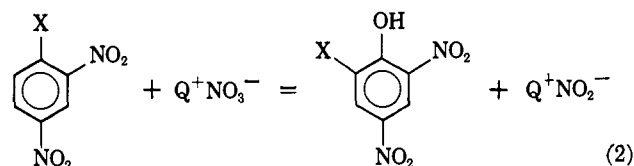
Results

2,4-Dinitrophenyl Derivatives. 2,4-Dinitrobromobenzene is not affected by treatment for 3 hr. with silver nitrate or tetra-*n*-hexylammonium nitrate in refluxing acetonitrile. However, it is 83% converted by molten tetra-*n*-hexylammonium nitrate, under the same conditions of temperature and time, to products derived from 2,4-dinitrophenol. The basic transformation observed with activated aryl halides and fused quaternary ammonium nitrates (hereafter $Q^+NO_3^-$) is



Results for these systems are given in Table I.

The reaction can be made to give either product in high yield (expt. 7 and 8). It has been established (expt. 1–7 and 15–20) that the reaction proceeds in two stages, one in which 1 is converted to the halophenol 2, and a second in which 2 is converted to the nitrophenol 3. This second stage was found to be duplicated⁴ with respect to product, by-products, qualitative rate, and visual appearance by the reaction (expt. 35–41) of halophenol 2 with molten nitrite, $Q^+NO_2^-$. The analogous transformation of some halophenols is known to be effected by nitrous acid solutions.⁵ The two stages are identified with reactions 2 and 3. The presence of nitrite in the reacting melt was chemically demonstrated (diazo coupling reaction).



Volatile intermediates can be swept from the reacting mixture by bubbling a stream of nitrogen through the melt. In the case of X = Br, NO, $NO_2-N_2O_4$, and NOBr were identified by infrared spectroscopy. These are, however, all characteristic of reaction 3, as a practically identical gas mixture was obtained independently from the bromophenol–nitrite reaction.

(4) The yield of 3 in the reaction of equimolar amounts of $Q^+NO_2^-$ and 2 (expt. 35 and 36) was not quite as great as that observed in the corresponding $Q^+NO_3^- + 1$ reaction (expt. 4). It was found that addition of 0.1 equiv. of $Q^+NO_3^-$ to the $Q^+NO_2^- + 2$ reaction mixture raised the yield markedly (expt. 37). Thus it is likely that in the $Q^+NO_3^- + 1$ reaction some nitrate is diverted to reaction 3. This also explains the presence of some unreacted 1.

(5) T. Zincke, *J. prakt. Chem.*, [2] 61, 561 (1900); L. C. Raiford and D. W. Kaiser, *J. Org. Chem.*, 4, 555 (1939).

(1) Part I: J. E. Gordon, *J. Am. Chem. Soc.*, 86, 4492 (1964).

(2) J. F. Bunnett, *Ann. Rev. Phys. Chem.*, 14, 281 (1963); A. J. Parker, *Quart. Rev.* (London), 16, 163 (1962).

(3) J. O. Edwards, *J. Am. Chem. Soc.*, 76, 1540 (1954); W. L. Petty and P. L. Nichols, Jr., *ibid.*, 76, 4385 (1954).

Table I. Reactions of 2,4-Dinitrophenyl Derivatives with Fused Quaternary Nitrates and Nitrite

Expt.	Substrate 	Reactants ^a		Additive	Conditions		Products, % ^c				Anal. method ^d
		Salt ^b			Temp., °C.	Time, min.					
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			80-120	90	?	25	68		Isol.
4	Br	Q ₅ NO ₃			107	120	7	16	77		N.m.r.
5	Br	Q ₅ NO ₃			100-120	150			77 ^e		Uv.
6	Br	Q ₅ NO ₃			100-120	150			64 ^e		Isol.
7	Br	Q ₅ NO ₃ (1.2)			107-125	180		6	86		Isol.
8	Br	Q ₅ NO ₃		Q ₆ Br	103-115	65		94	2		Isol.
9	Br	Q ₅ NO ₃ (3.0)			118	90		51	47		Isol.
10	Br	Q ₅ NO ₃		N ₂ -sweep	100-115	90		63	37		N.m.r.
11 ^f	Br	Q ₅ NO ₃		2,6-Dimethyl-phenol	110-120	130	49		10	39	Isol.
12	Br	AgNO ₃ or Q ₆ NO ₃		CH ₃ CN	82	180	~100				N.m.r.
12a	Br	Q ₆ NO ₃		CH ₃ CN	82	1020	89	9	~1		Isol.
13	Br	Q ₆ NO ₃			82	180	17	73	10		N.m.r.
14	Br	Q ₆ NO ₃			73	375		87	13		N.m.r.
15	Br	Q ₄ NO ₃ ^g			110	13	19	68	13		N.m.r.
16	Br	Q ₄ NO ₃			110	120	8	14	78		N.m.r.
17	I	Q ₅ NO ₃			105	5	>95				N.m.r.
18	I	Q ₅ NO ₃			105	13	53	47			N.m.r.
19	I	Q ₅ NO ₃			105	120	16	48	36		N.m.r.
20	I	Q ₅ NO ₃			108-120	120	?	41	38		Isol.
21	IO ₂	Q ₅ NO ₂ (2.0)			65-82	9	21	79			N.m.r.
22	IO ₂	Q ₅ NO ₂ (2.0)			60-120	60	13	73	14		N.m.r.
23	IO ₂	Q ₅ NO ₂ (2.0)			60-120	120		32	56		Isol.
24	Cl	Q ₅ NO ₃			109	13	>95				N.m.r.
25	Cl	Q ₅ NO ₃			100-115	240	~22	31	10	22	Isol.
26	OTs	Q ₅ NO ₃			104	5	~57 ^h		~43 ^h	<5 ^h	N.m.r.
27	OTs	Q ₅ NO ₃			105	5	~49 ^h		~38 ^h	~13 ^h	N.m.r.
28	OTs	Q ₅ NO ₃		Picric acid (0.5)	105	5	~90 ^h		~1 ^h	~9 ^h	N.m.r.
29	OTs	Q ₅ NO ₃		Q ₅ NO ₂ (0.1)	105	5	~44 ^h		~51 ^h	~5 ^h	N.m.r.
30	OTs	Q ₅ NO ₃			104	30	~37 ^h		~53 ^h	~10 ^h	N.m.r.
31	OTs	Q ₅ NO ₃ (1.1)			108	120	<26 ^h		~66 ^h	~8 ^h	N.m.r.
32	OTs	Q ₅ NO ₃ (1.1)			107-110	120	13		61	19	Isol.
33 ⁱ	OTs	Q ₅ NO ₃ (1.1)		N ₂ -sweep	107-110	120	<14		56	22	Isol.
34 ^j	OTs	Q ₅ NO ₃ (1.1)		2,6-Dimethyl-phenol	110-120	120			3	82	Isol.
35		Q ₅ NO ₂			95-115	120		28	66		Isol.
36		Q ₅ NO ₂			95-115	120		31	69		N.m.r.
37		Q ₅ NO ₂		Q ₅ NO ₃ (0.1)	105-120	120		6	94		N.m.r.
38		Q ₅ NO ₂ (1.2)			105-120	120			>95		N.m.r.
39		Q ₅ NO ₂ (1.2)			107-120	120		14	80		Isol.
40		Q ₅ NO ₂ (1.2)			107-120	120		8	80		Isol. ^k
41		Q ₅ NO ₂			100	120		74	24		Isol.
42		NaNO ₂		HOAc	12	60		99	0		Isol.
43		Q ₅ NO ₂ (1.1)			95-120	195		70	9		Isol.
								(91)	(9)		(N.m.r.)
44		Q ₅ NO ₂ (1.2)			85-120	120		9		32	Isol.
45 ^{l,m}		Q ₅ NO ₃		Q ₅ Br	100-120	60		78		22	N.m.r.
46		Q ₅ NO ₃		Q ₅ Br in MeCN	82	840				~100	N.m.r.

^a Mole ratio of salt and additive to substrate 1.0 unless otherwise given in parenthesis. ^b Q₅ = tetra-*n*-pentylammonium, Q₄ = tetra-*n*-butylammonium, etc. ^c The dinitrophenols were present in the untreated reaction product principally as the free phenols, and picric acid principally as picrate ion, as judged from the n.m.r. spectra. Whenever ambiguity arose in identifying lines due to phenol-phenoxide mixtures, the assignments were checked by adding trifluoroacetic acid and finding a shift to the pure phenol line positions. ^d Uv. = ultra-violet spectroscopy; isol. = chromatography, extraction, and weighing. In some cases the product composition is slightly altered during the chromatographic work-up (e.g., expt. 38 vs. 39 and 40; see ref. 16. ^e As Q₅⁺picrate⁻. ^f 4-Nitro-2,6-dimethylphenol (4%) also isolated. ^g Distillation Products Industries No. 9999. ^h Approximate values due to coincidence of some 2,4-dinitrophenol lines with those of ArOTs and OTs⁻; some of these reaction mixtures contained smaller amounts (<5%) of unidentified materials; these were ignored in arriving at the figures given. ⁱ Nitrogen(IV) oxide isolated (36%). ^j 4-Nitro-2,6-dimethylphenol (29%) also isolated. ^k Crude product in benzene treated with sodium hydrosulfite before chromatography. ^l Repetition of this experiment in concentrated aqueous solution resulted in no detectable conversion to 2. ^m Nitrite was formed (diazo coupling reaction).

The products of the nitrate-1 reaction with nitrogen sweep (expt. 10) show that the removal of gases has interfered with reaction 3 but not with reaction 2.

A reasonable working hypothesis for the detailed course of reaction 2 is (a) displacement of halide by an oxyanion, (b) oxidation of halide, and (c) halogenation of the dinitrophenol nucleus.

The reaction of 2,4-dinitrophenyl *p*-toluenesulfonate with molten nitrate allows observation of the formation and decomposition of the hypothesized initial intermediate in the absence of readily oxidized anions. The result is rapid formation of picric acid (expt. 26-32) accompanied by some 2,4-dinitrophenol. Gas swept from the reaction mixture (expt. 33) is essentially pure nitrogen(IV) oxide; the product composition under these purging conditions is not greatly altered. A certain degree of irreproducibility is observed in this reaction (e.g., expt. 26,27), possibly the product of adventitious moisture.

In both the bromide and tosylate reactions 1 molar equiv. of 2,6-dimethylphenol serves as a very efficient agent in intercepting some intermediate and diverting the reaction from formation of bromophenol (2) and picric acid (3) (expt. 11 and 34). Dinitrophenol is formed, but the products derived from the 2,6-dimethylphenol are largely tars, only small amounts of 4-nitro-2,6-dimethylphenol being isolated.

The reaction of 2,4-dinitroiodobenzene (expt. 17-20), although slower and less complete, is quite analogous to that of the bromo compound. With the chloro compound, which is still more inert, the reaction becomes more complex (expt. 24-25). Dinitrophenol appears as a product, and, in addition to NO, NO₂-N₂O₄, and NOCl, nitrous oxide is detected in the sweep gas. Presumably the less favorable oxidation of Cl⁻ is responsible for the inhibition of the previously observed reaction sequence.

Finally, the protection of bromophenol 2 by excess Q⁺Br⁻ which allows its isolation in very high yield (expt. 8) is accompanied by the appearance of larger amounts of NO in the sweep gas. Possibly the function of the Br⁻ is to reduce NO₂⁻.

o-Nitrobenzobenzene, 3-nitro-4-bromobenzoic acid, and 2-bromopyridine failed to react with Q⁺NO₃⁻.

Kinetic Measurements. The reaction of equimolar quantities of 1 and Q⁺NO₃⁻ was studied at 75° using tetra-*n*-hexylammonium nitrate. Under these conditions, formation of picric acid is eliminated up to at least 60% completion of reaction 2. Due to the fact that the reaction goes only to about 80% completion, and to the probable effects of changing medium, only qualitative significance can be expected, except possibly during the very early stages of the reaction. Plotted as a reaction first order in 1 and in Q⁺NO₃⁻ (1/X₁ - 1/X₁⁰ vs. time) the data produced the S-shaped curve, similar to that shown in Figure 1a, characteristic of an autocatalytic process. Addition of 10 mole % of Q⁺NO₂⁻ increased the initial rate by a factor of ~75 while a similar addition of the other reaction product (2) produced a *ca.* twofold rate decrease. The rate retardation by the phenol further complicates the reaction, and it is useless to attempt numerical analysis of the data. Some curves calculated from the rate law $d2/dt = kX_{\text{QNO}_2}X_1$ are plotted for comparison in Figure 1.⁶ The probable origin of the inhibition by

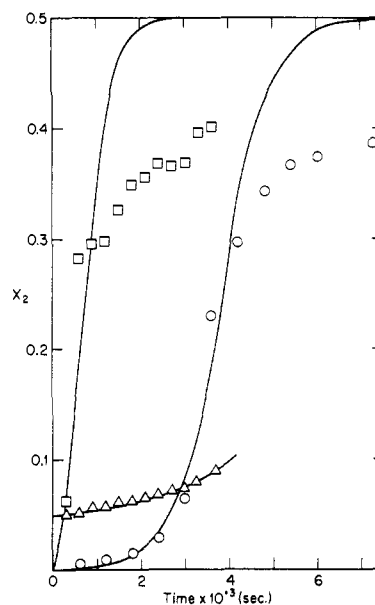
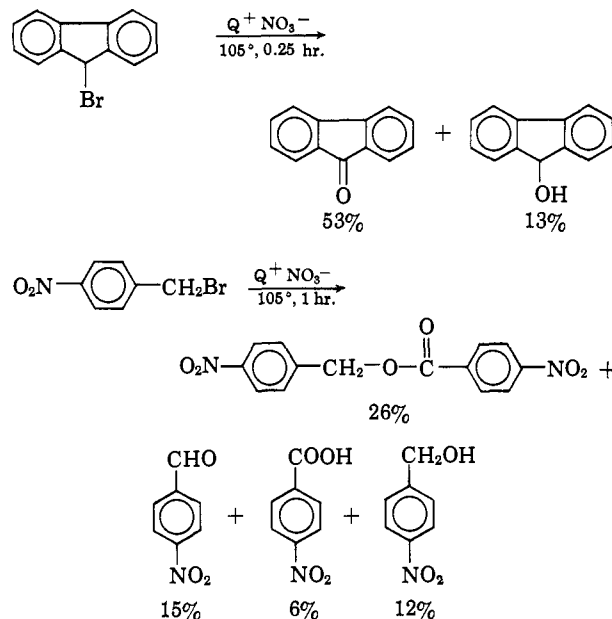


Figure 1. Kinetic data for Q₆NO₃ + 2,4-dinitrophenol at 75°; mole fraction of 2 plotted vs. time. ○: X₁⁰ = 0.500, X_{QNO₃}⁰ = 0.500; □: X₁⁰ = 0.500, X_{QNO₃}⁰ = 0.450, X_{QNO₂}⁰ = 0.050; △: X₁⁰ = 0.5006, X_{QNO₃}⁰ = 0.4504, X₂⁰ = 0.0490. The corresponding comparison curves were calculated from (X₁⁰ + X_{QNO₂}⁰)⁻¹ × ln (X_{QNO₂}X₁⁰/X_{QNO₃}⁰X₁) = *kt* with (a) *k* = 3.6 × 10⁻³ sec.⁻¹ and X_{QNO₂} = 5.0 × 10⁻⁴; (b) *k* = 6.6 × 10⁻³ sec.⁻¹ and X_{QNO₂}⁰ = 5.05 × 10⁻²; (c) *k* = 1.0 × 10⁻³ sec.⁻¹ and X_{QNO₂}⁰ = 7.8 × 10⁻³.

2 lies in the equilibrium⁷ Q⁺NO₂⁻ + ArOH ⇌ Q⁺ArO⁻ + HONO, which also presumably contributes through loss and decomposition of nitrous acid to the premature end of reaction 3 short of completion.

Other Halides. Both 9-bromofluorene and *p*-nitrobenzyl bromide react rapidly with molten Q⁺NO₃⁻ to produce various oxidized products.



(6) Of the possible origins of the reaction-inducing trace of nitrite (nitrite impurity in the Q⁺NO₃⁻, oxidizable organic impurities, or a very slow competing displacement of halide by nitrate ion as nucleophile), the last is considered the most likely.

(7) The p*K*_a of 2-bromo-4,6-dinitrophenol appears not to have been measured; however it probably lies within a p*K* unit of that of nitrous acid (3.4).

Reaction of 2-bromopropane with molten nitrate was complex. The products listed in Table II were determined by gas chromatography. Products of the complimentary $Q^+Br^- + 2$ -propyl nitrate reaction are also shown in Table II.

Table II. Reactions of 2-Propyl Derivatives^a

Products	Yield, % ^b	
	From RBr + QNO ₃ ^c	From RONO ₂ + QBr ^c
Propene	32	42
?	...	0.2
?	0.6	0.2
2-Propyl ether	2.8	2.3
2-Propyl nitrite	2.6	1.4
2-Bromopropane	21	28
Acetone	9.0	7.3
?	2.1	3.0
2-Propanol	24	9.4
2-Propyl nitrate	4.9	5.7
2-Nitropropane	0.6	0.5

^a In sealed tube, 3 hr. at 120–125°. ^b Mole % taken as proportional to peak area %. ^c Q = tetra-*n*-pentylammonium.

Iodoxy Compounds. In the reaction of 2,4-dinitroiodobenzene with $Q^+NO_3^-$ a further source of nitrite ion is conceivably available in the reaction $ArI + 2Q^+NO_3^- = ArIO_2 + 2Q^+NO_2^-$. It was of interest to see if this reaction occurs, for its own sake as well as in connection with the nitrite catalysis. Working with iodo- and iodoxybenzene where no displacement reactions occur, it was found that molten $Q^+NO_3^-$ does not oxidize ArI ; however, $Q^+NO_2^-$ efficiently reduces iodoxybenzene to iodobenzene. Thus the above equilibrium is well to the left. When 2,4-dinitroiodoxybenzene is treated with molten $Q^+NO_2^-$, the reaction mimics in every respect the $ArI-Q^+NO_3^-$ reaction, as expected, except that it is much faster at 65–82° than the latter at 105°. This is again evidence of nitrite catalysis. Started at higher temperatures, the $ArIO_2-Q^+NO_2^-$ reaction is explosive.

Discussion

2,4-Dinitrophenyl Derivatives. Reaction 2. An appealing interpretation of eq. 2 would begin with nucleophilic displacement of X^- by NO_3^- . Nearly all of the observations could be satisfactorily accounted for as proceeding from the reactive nitrate ester thus formed. However, since nitrite ion is a so much more reactive nucleophile toward such substrates than nitrate,³ it is essential to look for the possible occurrence, in this unfamiliar medium, of a catalytic oxidation-reduction mechanism in which nitrite is the effective nucleophile. The kinetic results, though crude, suffice to establish that nitrite is indeed performing this role.

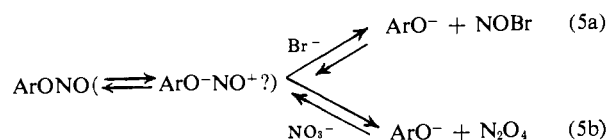


Aryl nitrites have apparently never been isolated.⁸

The 2,4-dinitrophenyl nitrite must be regarded as a potent nitrosating agent. Its lifetime in the reaction mixture is undoubtedly short. Infrared and n.m.r. spectra of the reacting melt give no evidence of an in-

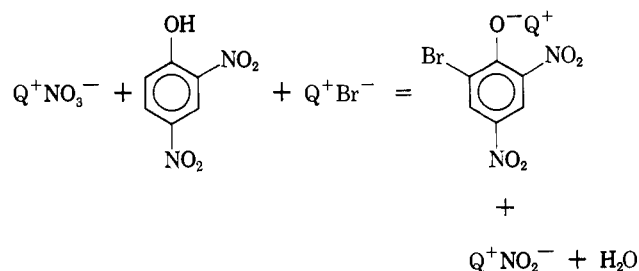
(8) Their possible intermediacy or transient occurrence in phenol nitration reactions has been mentioned: C. A. Bunton, *et al.*, *J. Chem. Soc.*, 2628 (1950); ref. 15, p. 149.

termediate between 1 and 2. Nitrosonium transfer equilibria are presumably established with the available nucleophiles, and it is likely that the ester is itself

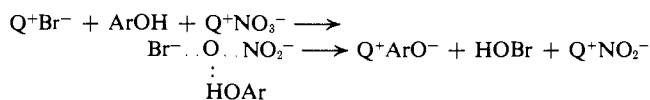


dissociated to some extent in the melt.⁹

In the reaction of the bromo compound, the next step must be oxidation of bromide.¹⁰ While the oxidizing agent could be nitrogen(IV) oxide, a nonvolatile oxidant perhaps accommodates better the fact that nitrogen purging of the reacting melt interferes with reaction 3 but not reaction 2. It was shown (expt. 45) that nitrate ion is itself surprisingly capable of rapidly oxidizing bromide in this medium in the presence of the relatively weak acid 2,4-dinitrophenol.



In water at 25° this oxidation is thermodynamically very unfavorable ($\Delta F \sim +18$ kcal./mole). The rate constant for the process $NO_3^- + H_3O^+ + Br^- = NO_2^- + HOBr + H_2O$ can be estimated from data of Lister and Rosenblum¹¹ on the reverse reaction for hypochlorite as $\sim 10^{-18}$ l. mole⁻¹ min.⁻¹. Only in relatively concentrated nitric acid is the reaction observed. Details on the oxidation in the fused salt (order in $ArOH$, general vs. specific acid catalysis) would be of interest. If the mechanism is analogous to that which appears likely^{11,12} for the aqueous $ClO^-NO_2^-$



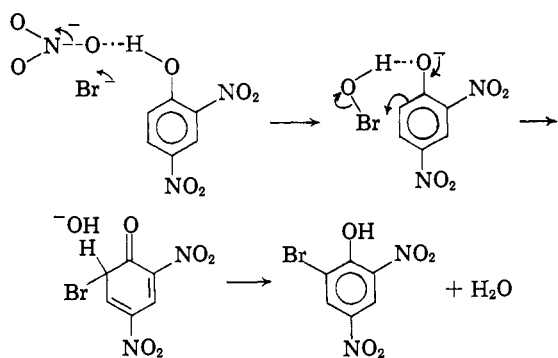
reaction, the change of medium has certainly enhanced the rate. The fused salt medium does indeed appear ideal in this respect, both in minimizing electrostatic effects in a poorly protonated anion-anion transition state and in providing high Br^- nucleophilicity. Such a mechanism, with $ArOH$ present as general acid in the transition state, also suggests the possibility that the bromination step might occur nearly synchronously with the Br^- oxidation. Such a concerted process cannot be essential to the oxidation, however, since one can trap Br_2 as stilbene dibromide on fusing QBr , QNO_3 , 2-bromo-4,6-dinitrophenol, and stilbene together.

(9) T. Moeller, *J. Chem. Educ.*, 23, 441 (1946); 24, 149 (1947).

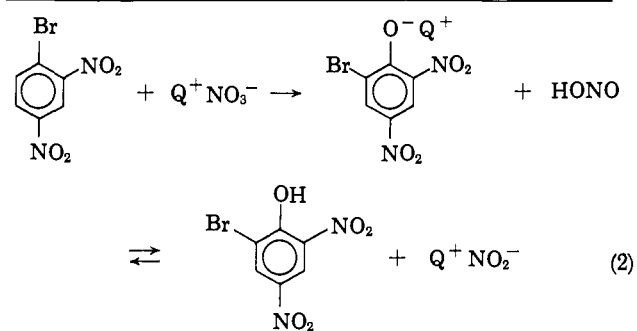
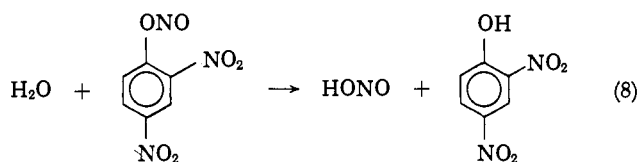
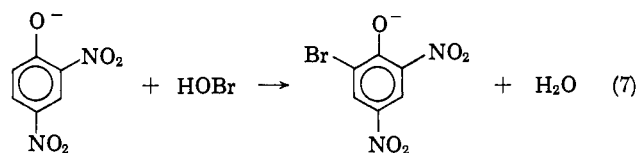
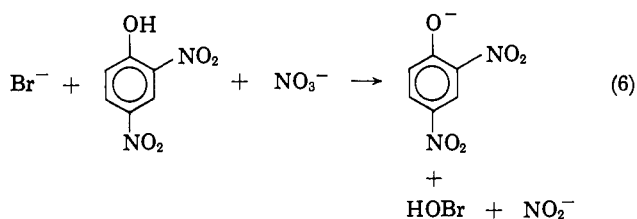
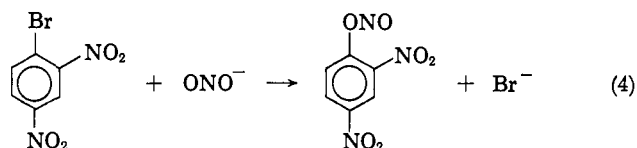
(10) Nitrosyl bromide, which functions as a nitrosating, not a brominating agent, is an unlikely intermediate.

(11) M. W. Lister and P. Rosenblum, *Can. J. Chem.*, 39, 1645 (1961).

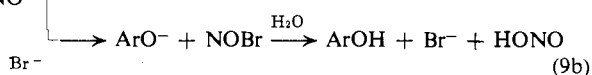
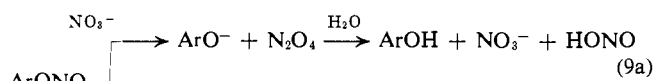
(12) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, pp. 88, 137 ff.; M. Anbar and H. Taube, *J. Am. Chem. Soc.*, 80, 1073 (1958).



Reaction 2 then can be most simply accounted for as the sum of

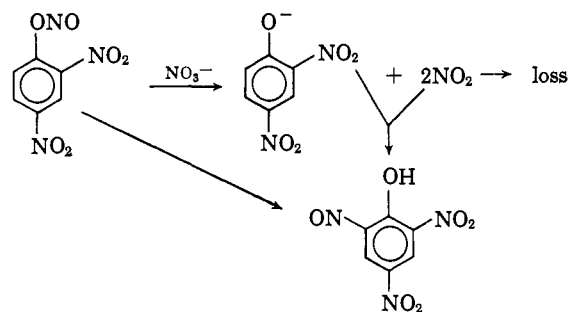


Reaction 8 need not literally occur. Other routes are available for destruction of the nitrite ester.



In the reaction of 2,4-dinitrophenyl tosylate, reaction 5b accounts for the observed (expt. 33) formation of nitrogen(IV) oxide. No intermediate, with the pos-

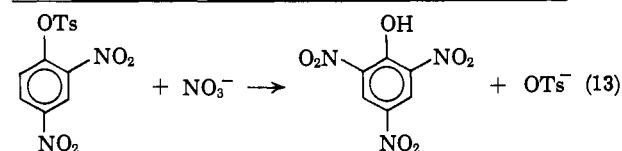
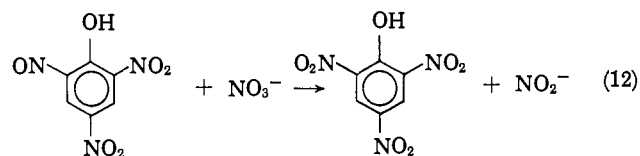
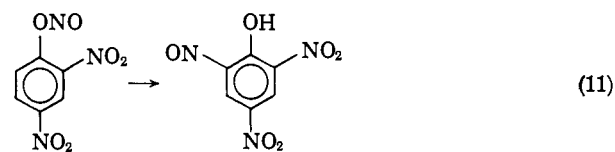
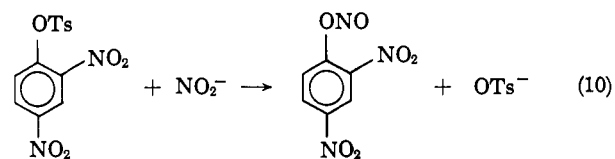
sible exception of 2,4-dinitrophenol, is detected (expt. 26-31) in the conversion of the tosylate to picric acid. Hypothesizing formation of the aryl nitrite intermediate as with the bromo compound, conversion to picric acid could proceed *via* 2,4-dinitrophenol and nitrogen(IV) oxide, or *via* intra- or intermolecular self-nitrosation followed by oxidation. Small amounts of 2,4-



dinitrophenol are detected in the reacting melt (expt. 26-31). The somewhat larger quantity (19-22%) isolated in expt. 32-33, appears to result from hydrolysis of unreacted starting tosylate in the chromatographic work-up. Since the picric acid yield drops by only 5% on purging nitrogen(IV) oxide from the reacting melt (expt. 33), it appears likely that the bulk of the reaction goes by way of direct nitrosation, the other path leading partly to picric acid (5-10%) and partly to loss of nitrogen(IV) oxide and formation of 2,4-dinitrophenol. In expt. 33 the picric acid and nitrogen(IV) oxide together account for 0.92 molar equiv. of the starting nitrate.

In view of the efficient interception of the picric acid forming reaction by 2,6-dimethylphenol (expt. 34), if the nitrite ester is to react intramolecularly, this must be a relatively inefficient intramolecular reaction.

A possible reaction sequence is

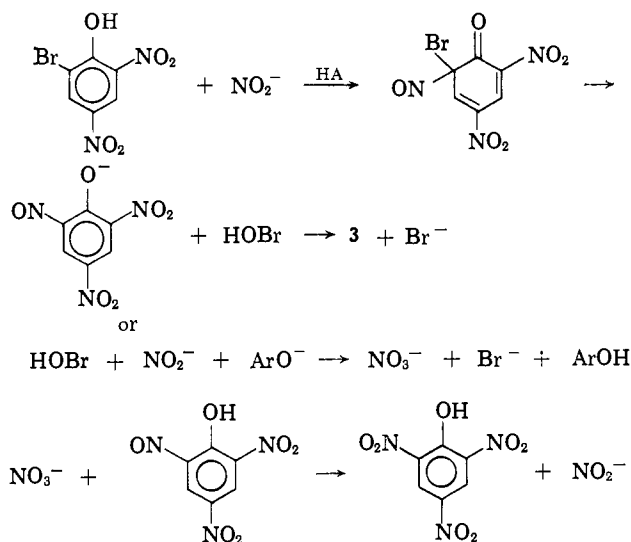


In support of (12), 1-nitroso-2-naphthol is known¹³

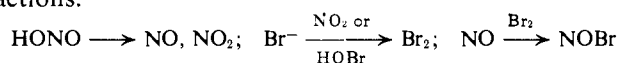
(13) J. B. Cohen and H. T. Calvert, *J. Chem. Soc.*, 71, 1050 (1897).

to be oxidized to the nitro compound by dilute aqueous nitric acid at room temperature. *p*-Nitroso-N,N-dimethylaniline reacts rapidly with molten $Q^+NO_3^-$ in the presence of benzoic acid at 115°. However, in this case only a few per cent of the nitro compound is isolated; the remainder of the material goes on to highly colored products. The tosylate- $Q^+NO_3^-$ reaction is not autocatalytic. Some evidence for the nitrite catalysis expressed in reactions 10–12 was obtained in expt. 28–29 which demonstrate some enhancement by added nitrite and the inhibiting effect of added picric acid (*cf.* 2,4-dinitrophenol- $Q^+NO_3^-$ reaction). The extent to which the alternative sequence—initial displacement by nitrate ion, aryl nitrate intermediate, direct aromatic nitration—may be participating is unknown, as is the source of possible nitrite catalyst.⁶ Since 2,4-dinitrophenyl tosylate reacts with piperidine as nucleophile about 25 times as rapidly as 2,4-dinitrophenol,¹⁴ the absence of NO_2^- autocatalysis and the greater reactivity in the tosylate case might together allow NO_3^- to play a substantial role as nucleophile.

Comparison of expt. 1 and 26–27 shows that although the disappearance of $ArBr$ proceeds faster than that of $ArOTs$, no rapid formation of picric acid corresponding to that observed for the tosylate occurs with the bromide. Hence reactions 6–8 are very efficient in diverting the aryl nitrite intermediate to formation of bromophenol (2). While there is no reason to consider this unlikely, it suggests an alternative explanation, namely that free aryl nitrite is never produced, the aromatic SN_2 intermediate decomposing directly to phenoxide and nitrosyl compound. The reaction



The volatile side reaction products could arise from thermal decomposition of nitrous acid and further reactions.



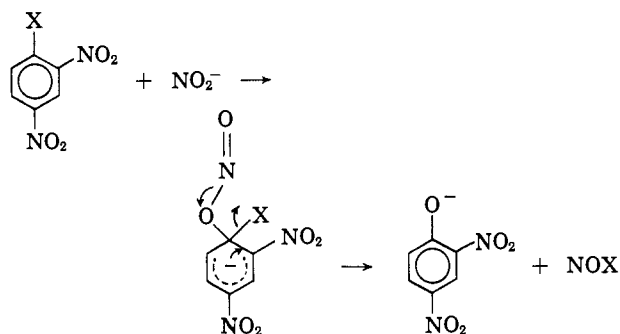
Several modifications of the fused $Q^+NO_2^-$ reaction were tried and are given in Table I (expt. 35–41).¹⁶ Comparison of the two methods is possible on several points. (1) The Zincke procedure is without effect on the deactivated 2-bromo-4,6-dinitrophenol (expt. 42); the $Q^+NO_2^-$ fusion is clearly advantageous here. (2) Chlorophenols generally do not give the Zincke reaction. $Q^+NO_2^-$ fusion of 2-chloro-4,6-dinitrophenol gave 9% of picric acid; less strongly deactivated chlorophenols were not tried. (3) With both procedures, hydrogen in a free *ortho* or *para* position is replaced in preference to bromine (expt 44; ref. 5).

Experiments in Solution. Although the processes are too slow to be of practical use, it was possible to show that small amounts of 2 and 3 are formed on prolonged refluxing of solutions of 1 and QNO_3 in acetonitrile (expt. 12a). Thin layer chromatography of the reacting solution gave evidence for the appearance of traces of picric acid after 3 hr., with 2 appearing only after 6 hr. The n.m.r. spectrum of the product after 12 hr. contained some very weak lines not due to 1, only some of which were attributable to 2. A more decisive reason for believing that the mechanism of formation of 2 in this system is more complex than that in the melt is the fact that, under the conditions of expt. 12a, reactions 6 and 7 do not occur detectably; no 2 is formed from QNO_3 , QBr , and 2,4-dinitrophenol in acetonitrile (the n.m.r. spectrum is capable of readily detecting and determining 2 at the level found in expt. 12a—*e.g.*, for a synthetic mixture, % 2 calcd.: 9.0; found: 10.3).

Other Halides. The reactions of the alkyl and aralkyl bromides with molten $Q^+NO_3^-$ are understandable in

(16) The isolation procedure employed (liberation of phenols with trifluoroacetic acid and chromatography away from Q^+ salts) often afforded significantly less nitrophenol than was known to be present in the raw product. This appears to be due to oxidation of bromide and reversal¹⁷ of (3) during the chromatography; destruction of nitrite with urea before chromatography appeared helpful, but was not thoroughly investigated.

(17) Bromine is known to convert 3 to 2: W. Mac Karrow, *Ber.*, 24, 2939 (1891).



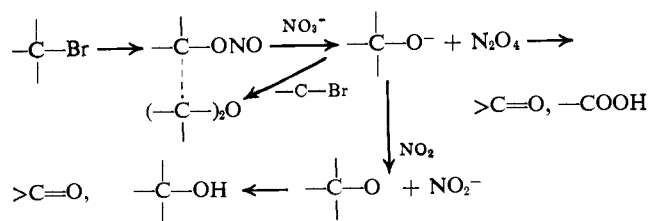
sequences could then be completed by (6), (7), and (9b) on the one hand and (9a) together with NO^+ nitrosation and (12) on the other. In this case the nitrosating reactivities of $NOBr$ and the hypothetical NO^+OTs^- might be expected to differ widely.

2,4-Dinitrophenyl Derivatives. Reaction 3. Reaction 3 and the analogous nitrodehalogenation⁵ of bromophenols by nitrous acid in acetic acid near room temperature are presumably nitrosation-oxidation reactions.¹⁵ All observations on the reactions are accountable in this way. A possible sequence for reaction 3 is

(14) J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, *J. Am. Chem. Soc.*, 79, 385 (1957).

(15) P. B. D. De La Mare and J. H. Ridd, "Aromatic Substitution. Nitration and Halogenation," Butterworth and Co. (Publishers) Ltd., London, 1959, Chapter 7.

terms of the foregoing discussion, the behavior of analogous intermediates in nitrite pyrolysis,¹⁸ and the



known oxidation of alcohols by nitrogen(IV) oxide.¹⁹ Propylene may arise in the reaction of 2-bromopropane by a direct E2 process. The Q^+Br^- -2-propyl nitrate reaction appears to proceed *via* $Q^+NO_3^-$ and 2-bromopropane.²⁰

Experimental²¹

Tetra-*n*-pentylammonium Nitrate. A solution of 3.398 g. (0.02 mole) of silver nitrate in 10 ml. of 75% ethanol was added dropwise to a stirred solution of 8.510 g. (0.02 mole) of tetra-*n*-pentylammonium iodide (Distillation Products Industries) in 150 ml. of ethanol. Stirring was continued for 2 hr. The silver iodide was filtered off and washed with ethanol, and the filtrate was evaporated at reduced pressure to a white solid which was recrystallized twice from ethyl acetate-ethyl ether giving 6.766 g. (0.0188 mole, 94%) of the nitrate, m.p. 112.5-113.5° (lit.²³ m.p. 115-115.5°).

Anal. Calcd. for $C_{20}H_{44}N^+NO_3^-$: NO_3^- , 17.20. Found²⁴: NO_3^- , 17.10.

Tetra-*n*-pentylammonium Nitrite. A suspension prepared from 21.28 g. (0.05 mole) of tetra-*n*-pentylammonium iodide, 8.465 g. (0.055 mole) of silver nitrite (Fisher purified), 340 ml. of ethanol, and 100 ml. of water was stirred under nitrogen in the dark for 22 hr. The solid was filtered off and washed with ethanol; the filtrate was evaporated at reduced pressure to a white solid which was recrystallized three times from ethyl acetate-ethyl ether giving 14.35 g. (0.0416 mole, 83%) of tetra-*n*-pentylammonium nitrite, m.p. 95-

(18) A. L. Nussbaum and C. H. Robinson, *Tetrahedron*, **17**, 35 (1962).

(19) J. L. Riebsomer, *Chem. Rev.*, **36**, 157 (1945).

(20) F. L. M. Pattison and G. M. Brown, *Can. J. Chem.*, **34**, 879 (1956).

(21) Experiments representative of each system studied are described; results of duplicate experiments and minor modifications are given in Table I. Parenthesized numbers following section headings indicate the experiments of Table I to which the procedure applies (with the exception of work-up or analytical procedure as noted in the table). Infrared spectra were recorded on a Perkin-Elmer Model 21 instrument with sodium chloride optics; electronic spectra were recorded on a Cary Model 14 instrument. N.m.r. spectra were measured on a Varian A-60 spectrometer. Analyses of mixtures *via* n.m.r. were performed on solutions in 0.35 ml. of acetonitrile of reaction products from ca. 150 mg. of substrate; the broadest possible display of the spectrum was recorded and integrated with a planimeter. Melting points were measured on a Kofler hot-stage microscope and are corrected. Combustion analyses were performed by Galbraith Laboratories, Inc. Whether explicitly stated or not, identity of all products isolated was checked by either mixture melting point or identity of infrared or n.m.r. spectra with authentic specimens. Infrared gas spectra were identified by comparison with authentic specimens and published spectra.²²

(22) R. H. Pierson, A. N. Fletcher, and E. St. C. Gantz, *Anal. Chem.*, **28**, 1218 (1956); W. G. Burns and H. J. Bernstein, *J. Chem. Phys.*, **18**, 1669 (1950).

(23) L. M. Tucker and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 454 (1947).

(24) By treatment with ion-exchange resin in the chloride state, followed by Volhard titration of Cl^- .

97.5°. The analytical sample was dried at room temperature and 10^{-4} mm.

Anal. Calcd. for $C_{20}H_{44}N_2O_2$: C, 69.71; H, 12.87; N, 8.13. Found: C, 69.89; H, 12.56; N, 8.05.

A second crop, m.p. 86-90°, 1.844 g. (0.0053 mole, 11%) was obtained.

Reaction of 2,4-Dinitrobromobenzene with Molten Nitrate. (a) (*Expt. 1-4, 6, and 9*) Tetra-*n*-pentylammonium nitrate (1.000 g., 2.77 mmole) and 2,4-dinitrobromobenzene (Distillation Products Industries, 0.685 g., 2.77 mmole) were heated together in an open flask for 1.5 hr. during which time the temperature was raised from 80 to 120°. The mixture was applied in 4 ml. of benzene-trifluoroacetic acid (3:1) to a 30-g. column of silicic acid; 350 ml. of benzene eluted 0.650 g. of pale yellow solid. Of this, 0.436 g. in 25 ml. of methylene chloride was extracted with 150 ml. of citrate buffer, pH 4.4, which was then extracted with three 25-ml. portions of methylene chloride; the organic portions were countercurrently equilibrated with 100 ml. of phosphate buffer, pH 8.0, dried over magnesium sulfate, and evaporated to 0.017 g. of yellow oil, not further investigated. From the pH 8 buffer there was obtained on acidification to pH 3.9 with citric acid and extraction 0.123 g. (0.468 mmole, 25%) of 2-bromo-4,6-dinitrophenol, m.p. (after crystallization from ethanol in 83% recovery) 116.5-118°, m.m.p. with an authentic specimen (m.p. 117.5-118°, lit.²⁵ m.p. 118°) prepared by bromination of 2,4-dinitrophenol, 117.5-118°, infrared spectrum identical with that of the latter. The pH 4.3 solution on acidification with 18 ml. of sulfuric acid yielded on extraction 0.288 g. (1.26 mmole, 68%) of picric acid, m.p. 120-121.5°, mixture melting point and infrared spectrum identical with an authentic specimen.

(b) (*Expt. 8*) A mixture of 0.342 g. (1.39 mmole) of 2,4-dinitrobromobenzene, 0.500 g. (1.39 mmole) of tetra-*n*-pentylammonium nitrate, and 0.525 g. (1.39 mmole) of tetra-*n*-pentylammonium bromide was heated for 1.1 hr. at 103-115°. Of the resulting 1.330 g. of red oil, 0.665 g. was put through the above chromatography-extraction work-up giving 0.172 g. (0.654 mmole, 94%) of 2-bromo-4,6-dinitrophenol and 0.007 g. (0.03 mmole, 2%) of picric acid.

(c) (*Expt. 7*) After heating a mixture of 0.245 g. (1.00 mmole) of 2,4-dinitrobromobenzene and 0.433 g. (1.20 mmole) of tetra-*n*-pentylammonium nitrate for 3 hr. at 107-125°, the above work-up provided 0.198 g. (0.865 mmole, 86%) of picric acid and 0.016 g. (0.061 mmole, 6%) of 2-bromo-4,6-dinitrophenol.

(d) (*Expt. 5*) From 0.685 g. (2.77 mmole) of 2,4-dinitrobromobenzene and 1.000 g. (2.77 mmole) of tetra-*n*-pentylammonium nitrate, heated for 2.5 hr. at 100-120°, was obtained 1.576 g. of orange solid. A 1.387-g. aliquot was chromatographed on 25 g. of silicic acid. After 0.088 g. of yellow oil, the main fraction consisting of 0.971 g. of yellow solid was eluted with 600 ml. of chloroform; this was followed by 0.078 g. of intermediate and 0.119 g. (0.314 mmole, 13%) of tetra-*n*-pentylammonium bromide eluted with chloroform-ethanol (1-4%). The main fraction was re-chromatographed on 25 g. of silicic acid to give 0.815

(25) R. L. Datta and J. C. Bhoomik, *J. Am. Chem. Soc.*, **43**, 303 (1921).

g. (1.54 mmoles, 64%) of tetra-*n*-pentylammonium picrate, as a chloroform and chloroform-0.5% ethanol eluted fraction, m.p. and m.m.p. with an authentic sample 73-74.5°.

Reaction of 2,4-Dinitrobromobenzene with Molten Nitrate in the Presence of 2,6-Dimethylphenol (Expt. 11). 2,4-Dinitrobromobenzene, 0.342 g. (1.38 mmoles), 2,6-dimethylphenol, 0.170 g. (1.39 mmoles, Distillation Products Industries, recrystallized from pentane, m.p. 45-47°), and tetra-*n*-pentylammonium nitrate, 0.500 g. (1.39 mmoles), were heated together at 110-120° for 1.2 hr. The resulting black oil was chromatographed as in (a) above; gas evolution on the column caused channelling and the 0.495 g. of material eluted with 300 ml. of benzene was rechromatographed, 0.324 g. of material being eluted with 350 ml. of benzene. This was separated by extraction as before into a *pK* ~ 0.5 fraction (picric acid, 0.032 g., 0.14 mmole, 10%), a *pK* ~ 4 fraction (2,4-dinitrophenol, 0.098 g., 0.53 mmole, 39%, m.p. 110-112° after sublimation on the hot stage, identified by the n.m.r. spectrum) and a *pK* > 4 fraction, 0.192 g. The latter was separated by distribution between methylene chloride and pH 10 phosphate buffer into 0.009 g. (0.05 mmole, 4%) of 4-nitro-2,6-dimethylphenol (m.p. 165-170° sub. and dec., identified by identity of the infrared spectrum with authentic material, m.p. 172.5-173°, prepared by nitration of 2,6-dimethylphenol), and 0.168 g. (0.680 mmole, 49%) of recovered 2,4-dinitrobromobenzene. It was independently established that 2-bromo-4,6-dinitrophenol is not directly debrominated by 2,6-dimethylphenol under the reaction conditions.

Reaction of 2,4-Dinitrobromobenzene with Quaternary Nitrate in Acetonitrile (Expt. 12a). 2,4-Dinitrobromobenzene, 0.370 g. (1.50 mmoles), and tetra-*n*-pentylammonium nitrate, 0.5415 g. (1.50 mmoles), were dissolved in 6 ml. of acetonitrile and the solution was refluxed for 17 hr., then evaporated at room temperature. The resulting solid was treated as in (a) above. The neutral fraction was 0.329 g. (89%) of recovered starting material. From the pH 4 extracts was obtained 0.004 g. (1%) of yellow solid with the infrared spectrum of picric acid. The pH 8 extracts afforded 0.035 g. (0.13 mmole, 8.9%) of 2-bromo-4,6-dinitrophenol, m.p. 115-117°, m.m.p. 116-118°.

Reaction of 2,4-Dinitroiodobenzene with Molten Nitrate (Expt. 17-20). Heating a mixture of 0.441 g. (1.50 mmoles) of 2,4-dinitroiodobenzene (Aldrich Chemical Co., m.p. 87-89°) and 0.542 g. (1.50 mmoles) of tetra-*n*-pentylammonium nitrate for 2 hr. at 108-120° produced a dark oil which was worked up as described for the bromo compound (section a) above. The first chromatographic fraction contained free iodine. The pH 8 extracts provided 0.192 g. (0.620 mmole, 41%) of 2-iodo-4,6-dinitrophenol, m.p. 93-95²⁶ and 103-105°, m.m.p., with a sample prepared from dinitrophenol, iodine, and iodic acid (m.p. 106-107.5°, lit.²⁶ m.p. 106°), 104-106°. Picric acid, 0.130 g. (0.568 mmole, 38%), m.p. 119-121.5°, was obtained from the pH 4 extract.

Reaction of 2,4-Dinitroiodoxybenzene with Molten Nitrite (Expt. 21-23). 2,4-Dinitroiodoxybenzene, pre-

pared according to Lütgert²⁷ (0.245 g., 0.752 mmole), and tetra-*n*-pentylammonium nitrite (0.517 g., 1.50 mmoles) were mixed and heated slowly from 60 to 120° over 2 hr. Rapid heating results in an explosive reaction. Worked up as in the preceding section, the reaction mixture was in all respects visually similar to that from the nitrate-iododinitrobenzene reaction and gave 0.074 g. (0.24 mmole, 32%) of 2-iodo-4,6-dinitrophenol, m.p. and m.m.p. 105-106.5°, and 0.096 g. (0.42 mmole, 56%) of picric acid, m.p. 118-121°.

Reaction of Iodoxybenzene with Molten Nitrite. A mixture of 0.177 g. (0.75 mmole) of iodoxybenzene (K and K Laboratories) and 0.516 g. (1.5 mmoles) of tetra-*n*-pentylammonium nitrite was heated for 2.5 hr., the temperature being raised from 90 to 120° during this period. The mixture was treated with acetonitrile and filtered; 0.013 g. (7%) of solid iodoxybenzene was recovered and the filtrate possessed the n.m.r. spectrum of pure iodobenzene. Iodobenzene failed to react with the molten nitrate in 3 hr. at 110° (n.m.r.).

Reaction of 2,4-Dinitrochlorobenzene with Molten Nitrate (Expt. 24 and 25). A mixture of 0.562 g. (2.77 mmoles) of 2,4-dinitrochlorobenzene (Kahlbaum, recrystallized from ether, m.p. 50-51°) and 1.000 g. (2.77 mmoles) of tetra-*n*-pentylammonium nitrate was heated for 4 hr. during which time the temperature was raised from 100 to 115°. The resulting dark oil was applied to 15 g. of silicic acid in benzene-trifluoroacetic acid as before; the first 150 ml. of benzene effluent contained 0.506 g. of material which was fractionated by extraction as previously described into a 0.123-g. neutral fraction with the n.m.r. spectrum of the starting material, 0.066 g. (0.29 mmole, 10%) of picric acid, and 0.298 g. of a mixture of 2,4-dinitrophenol and 2-chloro-4,6-dinitrophenol which was identified by comparison of the n.m.r. spectrum with spectra of authentic samples. Analysis by integration of the n.m.r. spectrum gave: 2,4-dinitrophenol, 0.111 g., 0.604 mmoles, 22%; 2-chloro-4,6-dinitrophenol, 0.187 g., 0.855 mmole, 31%.

Reaction of 2,4-Dinitrophenyl p-Toluenesulfonate with Molten Nitrate. (a) (Expt. 26-32) A mixture of 0.338 g. (1.00 mmole) of 2,4-dinitrophenyl tosylate (m.p. 119.5-120°, prepared according to Freudenberg and Hess²⁸) and 0.397 g. (1.10 mmoles) of tetra-*n*-pentylammonium nitrate was heated for 2 hr. at 107-110°. The resulting red oil was processed by the chromatography-extraction procedure described above, giving 0.044 g. (0.13 mmole, 13%) of recovered starting tosylate, m.p. 105-120° (n.m.r. spectrum identical with the starting material), 0.035 g. (0.19 mmole, 19%) of 2,4-dinitrophenol, m.p. 112-113.5°, infrared spectrum and mixture melting point identical with authentic material, and 0.140 g. (0.611 mmole, 61%) of picric acid, m.p. 120.5-122°.

(b) (Expt. 33) Repetition of the preceding experiment while sweeping a stream of dry nitrogen through the melt afforded 22% of 2,4-dinitrophenol and 56% of picric acid. The exit gas was passed through a liquid nitrogen cooled trap and the condensate was transferred on the vacuum line to a 10-cm. path infrared

(26) H. E. Armstrong, *Ber.*, **6**, 649 (1873). The 95° modification appears not to have been previously described.

(27) H. Lütgert, *ibid.*, **70**, 151 (1937).

(28) K. Freudenberg and H. Hess, *Ann.*, **448**, 121 (1926).

cell. The infrared spectrum observed was that of the nitrogen(IV) oxides with an additional unidentified band at 790 cm^{-1} . A third, identical experiment was conducted in which the nitrogen sweep gas was passed not through a cold trap but into water; titration of the resulting acid solution required 0.237 mequiv. of alkali, corresponding to 0.356 mmole (36%) of nitrogen dioxide.

Reaction of 2,4-Dinitrophenyl p-Toluenesulfonate with Molten Nitrate in the Presence of 2,6-Dimethylphenol (Expt. 34). In a sealed ampoule, 0.338 g. (1.00 mmole) of 2,4-dinitrophenyl tosylate, 0.122 g. (1.00 mmole) of 2,6-dimethylphenol, and 0.397 g. (1.10 mmoles) of tetra-*n*-pentylammonium nitrate were heated at 110–120° for 2 hr. The dark, oily product was chromatographed on 11 g. of silicic acid as before; 100 ml. of benzene eluted fraction A, 0.169 g. of pale yellow solid, followed by 0.048 g. (0.288 mmole, 29%) of 4-nitro-2,6-dimethylphenol, m.p. 170–173°, mixture melting point identical with that of the authentic material. This was followed by 0.037 g. of rapidly decomposing solids. Fraction A was put through the previously described extraction procedure giving 0.151 g. (0.821 mmole, 82%) of 2,4-dinitrophenol, m.p. and m.m.p. 112–113.5°, and picric acid, 0.008 g. (0.03 mmole, 3%), m.p. 114–121°, identified by its infrared spectrum.

Reaction of 2-Bromo-4,6-dinitrophenol with Molten Nitrite (Expt. 35–41 and 43). A mixture of 0.237 g. (0.901 mmole) of 2-bromo-4,6-dinitrophenol and 0.373 g. (1.08 mmole) of tetra-*n*-pentylammonium nitrite was heated at 107–120° for 2 hr. Worked up as for the bromide–nitrate reaction (section a), the product gave 0.166 g. (0.725 mmole, 80%) of picric acid, m.p. 120–121.5°, and 0.033 g. (0.12 mmole, 14%) of recovered bromophenol, m.p. 115–117°.

Reaction of 2-Bromo-4,6-dinitrophenol with Sodium Nitrite in Acetic Acid (Expt. 42). During 1 hr., sodium nitrite (0.164 g., 2.38 mmoles) was added in portions to a solution of 0.207 g. (0.787 mmole) of 2-bromo-4,6-dinitrophenol in 4 ml. of acetic acid at ~12°. After standing overnight at room temperature, the mixture was evaporated at reduced pressure and worked up by the extraction procedure previously described. Less than 0.001 g. of picric acid was obtained, and the $\text{pK} \sim 4$ fraction was pure recovered starting material (n.m.r. and m.p. 117–119°), 0.205 g. (99%).

Reaction of p-Bromophenol with Molten Nitrite (Expt. 44). A mixture of 0.173 g. (1.00 mmole) of *p*-bromophenol (Aldrich Chemical Co.) and 0.414 g. (1.20 mmoles) of tetra-*n*-pentylammonium nitrite was placed in a bath at 85° and heated for 2 hr. while the temperature was raised to 120°. The resulting oil was dissolved in 2 ml. of benzene and treated with 1 ml. of trifluoroacetic acid containing 0.120 g. of urea, followed by 0.5 ml. of cyclohexene; the resulting solution was chromatographed on 11 g. of silicic acid. With 150 ml. of benzene, 0.149 g. of material was eluted which was dissolved in methylene chloride and extracted successively with aqueous buffers of pH 4.2, 7.1, and 10 followed by 0.1 *N* sodium hydroxide. The unextracted neutral fraction weighed 0.003 g. No trace of picric acid or 2,4-dinitrophenol was obtained from the pH 4.2 and 7.1 solutions. The pH 10 solution was adjusted to pH 6.8; extraction afforded 0.084 g. of yellow solid shown by the n.m.r. spectrum to be a

mixture of *p*-bromophenol (0.015 g., 0.089 mmole, 9%) and 2-nitro-4-bromophenol (0.069 g., 0.315 mmole, 32%). Two recrystallizations from aqueous ethanol gave 2-nitro-4-bromophenol, 0.033 g., m.p. 86–89°, m.m.p. with authentic material (m.p. 88.5–89.5°) prepared according to Hübner,²⁹ 88–89°.

Oxidation of Bromide by Molten Nitrate (Expt. 45). A mixture of tetra-*n*-pentylammonium nitrate, 0.241 g. (0.667 mmole), tetra-*n*-pentylammonium bromide, 0.253 g. (0.667 mmole), 2-bromo-4,6-dinitrophenol, 0.175 g. (0.667 mmole), and *trans*-stilbene, 0.120 g. (0.667 mmole), was heated at 110° for 1 hr.; crystals appeared in the melt. The cooled mixture was treated with 0.5 ml. of acetonitrile and the solid product filtered off. The filtrate contained only bromodinitrophenol and stilbene (n.m.r.). The solid, 0.041 g. (0.12 mmole, 37%), m.p. 233° dec., was 1,2-dibromo-1,2-diphenylethane, infrared spectrum and melting point (238°), after recrystallization from xylene in 85% recovery, identical with those of an authentic specimen.

Kinetic Measurements. A 10-ml. erlenmeyer flask containing tetra-*n*-hexylammonium nitrate and any additive was brought to equilibrium in a rapidly stirred bath at 74.92 ± 0.02°. At zero time, finely powdered 2,4-dinitrobenzene (recrystallized three times from ethanol and sublimed at 10⁻⁴ mm.), which fused instantly, was added through a funnel; the melt was quickly mixed and the flask was lightly stoppered. At intervals, a length of 1-mm. capillary tubing was touched to the melt and a 9–12-mg. aliquot was removed and quenched in 25 ml. of a solution prepared by dissolving 1.210 g. of tris(hydroxymethyl)amino-methane (Sigma) in 50 ml. of water, adding 1 *N* hydrochloric acid to pH 8.1, and diluting to 1 l. with reagent methanol (Baker). These solutions were analyzed by measuring the optical density at 265.0 and 368.75 μ and employing the equations

$$E^{265} = 1.154 \times 10^4[1] + 6.121 \times 10^3[2]$$

$$E^{368.75} = 1.878 \times 10^2[1] + 1.707 \times 10^4[2]$$

Typical results for this analytical method, using synthetic mixtures of 1 and 2, are as follows. Calcd. (mole % 2-bromo-4,6-dinitrophenol): 5.35; 10.60. Found: 5.28; 10.58.

Reaction of 2-Bromopropane with Molten Nitrate. A mixture of 0.117 g. (0.952 mmole) of 2-bromopropane (Distillation Product Industries) and 0.361 g. (1.00 mmole) of tetra-*n*-pentylammonium nitrate was sealed with a break seal into a 2-ml. ampoule which was heated for 3 hr. at 120–125°. The seal was broken under vacuum and the volatile components were distilled into a cold trap and finally allowed to expand into a gas collection tube. This product mixture was analysed by gas-liquid chromatography on a column containing 15% polyethylene glycol 1500 on 60–80 mesh firebrick at 89°, giving the results shown in Table II. The results of reaction between 0.109 g. of 2-propyl nitrate (1.04 mmoles) and 0.379 g. (1.00 mmole) of tetra-*n*-pentylammonium bromide under the above conditions are also given in Table II. In addition to identity of retention times with authentic materials, the identification of each component was con-

(29) H. Hübner and O. Brenken, *Ber.*, 6, 170 (1873).

firmed by the infrared (gas phase) and/or n.m.r. (CDCl₃ solution) spectrum of the product mixture. The infrared spectrum of the product was completely accounted for by the components tabulated, with the exception of bands attributable to carbon dioxide and nitrous oxide.

Reaction of 9-Bromofluorene with Molten Nitrate. A mixture of 0.245 g. (1.00 mmole) of 9-bromofluorene (Matheson Coleman and Bell, recrystallized from hexane) and 0.361 g. (1.00 mmole) of tetra-*n*-pentylammonium nitrate was heated at 105° for 0.25 hr., cooled, and chromatographed in benzene on 11 g. of silicic acid. With 200 ml. of benzene, 0.177 g. of yellow solid (A) was eluted; 250 ml. of benzene then eluted 0.024 g. (0.13 mmole, 13%) of fluorenol, m.p. 155.5–157°, m.m.p. with an authentic sample (m.p. 156.6–158°) 155.5–157° after recrystallization from isooctane. Fraction A was rechromatographed in benzene–pentane (1:2) on 11 g. of silicic acid. After elution of 0.059 g. of unidentified solids with 600 ml. of solvent, an additional 350 ml. eluted 0.095 g. (0.53 mmole, 53%) of fluorenone, m.p. 71–72.5° or 84–85°,³⁰ infrared spectrum and mixture melting point identical with those of authentic material, m.p. 83.5–85°.

Reaction of *p*-Nitrobenzyl Bromide with Molten

(30) The various fractions crystallized either in modification I or II (L. Kofler and A. Kofler, "Thermo-Mikro-Methoden," Verlag Chemie, Weinheim, 1954, p. 419).

Nitrate. The orange oil obtained by heating 0.432 g. (2.00 mmoles) of *p*-nitrobenzyl bromide with 0.722 g. (2.00 mmoles) of tetra-*n*-pentylammonium nitrate for 1 hr. at 105° was dissolved in carbon tetrachloride. On cooling, *p*-nitrobenzyl *p*-nitrobenzoate, 0.077 g. (0.26 mmole, 26%), separated as white needles which were recrystallized from acetic acid in 94% recovery; m.p. 168°, resolidification, m.p. 171.5–172.5°, infrared spectrum and mixture melting point identical with those of an authentic specimen prepared according to Lyons and Reid³¹ (m.p. 168, 172.5–173.5°). The original carbon tetrachloride solution was evaporated and the residue was chromatographed on 12 g. of silicic acid. With 150 ml. of benzene 0.047 g. (0.31 mmole, 15%) of crude *p*-nitrobenzaldehyde, m.p. 70–97°, infrared spectrum identical with that of an authentic specimen, was eluted. After 0.011 g. of intermediate, 150 ml. of benzene and 350 ml. of benzene–chloroform (3:1) eluted 0.150 g. of a mixture from which 0.022 g. (0.13 mmole, 6%) of *p*-nitrobenzoic acid, identified by melting point (237–239°) and infrared spectrum, and 0.037 g. (0.24 mmole, 12%) of *p*-nitrobenzyl alcohol, m.p. and m.m.p. 91–93°, were obtained by crystallization from toluene and toluene–hexane.

Acknowledgment. The author thanks Drs. A. A. Bothner-By and E. Le Goff for helpful discussions.

(31) E. Lyons and E. E. Reid, *J. Am. Chem. Soc.*, **39**, 1727 (1917). Only the lower-melting modification was reported, m.p. 168.5°.

Studies of Ligand Transfer between Metal Halides and Free Radicals from Peroxides¹

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The role of ligand transfer in the catalytic decomposition of peroxides by metal species has been examined in the presence of halide salts. The catalytic reaction is generally clean; for example, valeryl peroxide and halide afford valerate, alkyl halide, and carbon dioxide in excellent yields. However, acyl peroxides are susceptible to nucleophilic attack by halide ions; and hypohalites formed as intermediates retard the chain decomposition of peroxides by copper salts by effectively scavenging the cuprous salts essential for the catalysis. The deleterious effect of these halogen-producing reactions to the catalytic process can be removed by the addition of reagents capable of quenching acyl hypochlorites and chlorine. The effectiveness of a reagent in this capacity, 1,3-dimethoxybenzene > styrene > octene-1 ≈ mesitylene ≈ anisole >> toluene, is related to its reactivity in electrophilic chlorination. Nucleophilic attack by bromide on peroxides is very rapid. Its contribution to the over-all decomposition of diacyl peroxides, however, is largely masked by a much more facile radical-chain com-

ponent in the presence of cupric bromide. The catalytic process with bromide, unlike chloride, is not substantially inhibited by molecular bromine due to the formation of cuprous bromide in equilibrium with bromine by disproportionation of cupric bromide in nonaqueous media. The formation of alkyl halides by ligand transfer in the free-radical chain decomposition of peroxides is retarded by oxygen. These reactions are compared to the copper-catalyzed decomposition of peroxides in the absence of halide.

Introduction

The decomposition of organic peroxides is markedly accelerated by small amounts of metal salts.^{2–4} Diacyl peroxides, peresters, and hydroperoxides are catalytically decomposed at temperatures lower than that required for the thermolysis. With aliphatic analogs, complications which often lead to a variety

(1) Part II. Reaction of Peroxides with Halides. Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

(2) J. K. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963).

(3) S. Goldschmidt, H. Späth, and L. Beer, *Ann.*, **649**, 1 (1962).

(4) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958); *J. Am. Chem. Soc.*, **81**, 2365 (1959).