A new method for the conversion of inorganic salts to the corresponding perchlorates

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NITROSYL perchlorate was found to react with inorganic salts, the anions of which form volatile nitrosyl compounds, to yield the solid, anhydrous metal perchlorates. This displacement reaction is believed to be of interest because it represents a new synthetic method of introducing the perchlorate group and possibly provides a relatively simple method of preparing various volatile nitrosyl compounds. In the experiments following, the salts KNO_3, KCl, NaF, $Ba(NO_3)_2$, and AgBr were reacted with nitrosyl perchlorate to give substantial conversions of the former materials to the corresponding perchlorates by the general, overall reaction:

$$MX_n \text{ (solid)} + nNOClO_4 \text{ (solid)} \rightarrow nNOX \text{ (gas)} + M(ClO_4)_n \text{ (solid)} \qquad (1)$$

The reported reaction(1) between silver perchlorate and nitrosyl chloride in a sealed tube producing silver chloride and nitrosyl perchlorate would appear to indicate that the displacement reactions of nitrosyl perchlorate might be of an equilibrium nature. Accordingly, in the present studies, reaction (1) was driven to the right by removal of the volatile reaction products from the reaction site.

Experimental Procedures and Results

The preparation of and analytical methods applied to nitrosyl perchlorate have been described in detail elsewhere.(2) (Chlorine: Found, 27·28%: Calc. for $NOClO_4$, 27·39%. Nitrosyl group: Found, 23·16%: Calc. for $NOClO_4$, 23·17%.) The additional salts used were all of reagent grade and were treated by drying at 110° for 12 hr prior to use.

The reaction mixtures (0·8 to 1·2 g) of Table 1 were prepared by mixing the components under anhydrous conditions. After standing for 24 hr in a tube vented through a drying tube filled with magnesium perchlorate, the resultant samples were heated at 50°, 75° and 100° for 4 hr periods at atmospheric pressure with venting of the gaseous reaction products; the samples were then heated under vacuum (3–5 mm Hg) for 3 hr, ground, and reheated under vacuum for 12 hr at 100°. Heating of the mixtures under vacuum conditions provided a convenient means for removing volatile nitrosyl compounds. Nitrosyl perchlorate itself undergoes thermal decomposition to gaseous products at elevated temperatures.(2,3,4) The results of chemical analyses of the final products are given in Table 1. Nitrosyl perchlorate was determined by reaction with excess sodium hydroxide solution and back-titration with standard acid.(2) Total chlorine was found by precipitation as silver chloride after fusion of the sample with sodium carbonate in a platinum crucible. Except for mixture (b), chlorine as chloride or chlorate was not present in any of the reaction residues.

In the instances of mixtures (a), (b) and (c), considerable reaction, as measured by weight losses, was noted to have occurred after standing at ambient temperature for 24 hr. Thus, 1·0138 g of (a) lost 0·1650 g; 0·7845 g of (b) lost 0·0691 g and 1·2456 g of (c) lost 0·0618 g. In an additional experiment 1·8549 g of a mixture containing 49·96 wt. % KNO_3 and 50·04 wt. % $NOClO_4$ underwent a weight loss of 0·1833 g after standing for one week in a vented tube at room temperature; 1·0004 g of nitrosyl perchlorate under similar conditions showed no change in weight after a three week period.

Discussion

Though pure metal perchlorates were not obtained in these studies, it is likely that prolongation of the reaction times at the lower temperatures, repeated grinding between heating periods, and longer evacuation intervals would have resulted in final products of greater purity.

The displacement behavior of nitrosyl perchlorate appears to be an example of a more general type

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TABLE 1.—SUMMARY OF RESULTS

Sample (MX_n)	Mole ratio $\frac{NOClO_4}{MX_n}$	$NOClO_4$ (wt. %)	Residue composition			
			$NOClO_4$ (wt. %)	MX_n (wt. %)	Cl (wt. %)	$M(ClO_4)_n$ (wt. %)
a (KNO_3)	1·852	70·33	6·85	2·02 (by diff.)	25·20	91·13
b (KCl)	0·946	62·15	1·80	1·14	25·54 (calc., 25·60	97·06 (by diff.)
c (KCl)	1·711	74·82	10·73	0·00	25·61 (calc., 25·79)	89·27 (by diff.)
d (NaF)	1·873	85·24	11·29	16·85 (by diff.)	23·90	71·86
e ($Ba(NO_3)_2$)	3·700	64·70	13·04	46·70 (by diff.)	11·85	39·26*
f (AgBr)	1·990	57·85	2·67 (by diff.)	3·77	—	93·56†

* Found 39·35%: Calc. Ba content of residue 40·58%.
† Based on water-soluble Ag content of 48·68%.

of reaction which may be characteristic of ionic or highly polar nitrosyl compounds. A number of examples involving other nitrosyl compounds are to be found in the literature:

$$NOBF_4 + NaF \rightarrow NOF + NaBF_4{}^{(5)} \qquad (2)$$

$$NOHSO_4 + NaCl \rightarrow NOCl + NaHSO_4{}^{(6)} \qquad (3)$$

$$NOCl + AgF \rightarrow NOF + AgCl^{(7)} \qquad (4)$$

$$\text{Nitrosation reactions in general:}^{(8,9)} \quad \text{Aryl: } H + NO^+ \rightarrow \text{Aryl : } NO + H^+ \qquad (5)$$

The nitrosyl perchlorate reactions described here bear a formal analogy to those displacement reactions involving condensed phases as reported by HEDVALL(10,11) to occur between metal oxides and metal salts (e.g. $MO + M'X \rightarrow MX + M'O$, where $X = CO_3, SO_4, SiO_3$, Cl or S). The negative values for the free energy changes of these reactions are due primarily to their exothermic nature. The nitrosyl perchlorate reactions, however, have been computed to be endothermic(12) and must proceed because of favourable entropy changes.

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