133. *Some Reactions of Anhydrous Perchloric Acid and Anhydrous Nitric Acid.*

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The reactions of anhydrous perchloric acid and anhydrous nitric acid with some anhydrous transition-metal chlorides have been examined. Perchloric acid with ferrous or ferric chloride gives ferric perchlorate dihydrate, while nitric acid has been shown to be more reactive, giving a series of hydrated transition-metal nitrates. The formation of the hydrated salts in these reactions has been explained by assuming the presence of the following equilibria in the anhydrous acids: $2HClO_4 \rightleftharpoons Cl_2O_7 + H_2O$; $2HNO_3 \rightleftharpoons N_2O_5 + H_2O$. Anhydrous perchloric acid has been shown to react with anhydrous metal nitrates thus: $MNO_3 + 3HClO_4 \longrightarrow MClO_4 + NO_2{\cdot}ClO_4 + H_3O{\cdot}ClO_4$. This reaction goes to completion with potassium nitrate, but is only 80—90% complete with transition-metal nitrates. As above, the transition-metal ions abstract water from the perchloric acid to yield the partially hydrated perchlorates and not the anhydrous salts.

ANHYDROUS perchloric acid is a potential reagent for the preparation of transition-metal perchlorates by the reaction:

$$MX_n + nHClO_4 \longrightarrow M(ClO_4)_n + nHX \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

and we have investigated some reactions in which X is chloride or nitrate.

A. THE REACTION OF ANHYDROUS PERCHLORIC ACID WITH SOME ANHYDROUS TRANSITION-METAL CHLORIDES.

Apparatus.—This consisted of a B.24 ground-glass joint connected to a solid carbon dioxide trap, followed by a U-tube containing solid potassium hydroxide, a liquid-air trap, and a vacuum-pump.

Transition-metal Chlorides.—An excess (4 ml.) of anhydrous perchloric acid, cooled to −80°, was pipetted on to ~1 g. of the anhydrous transition-metal chloride contained in a B.24 ground-glass tube cooled in solid carbon dioxide. The tube was then quickly attached to the apparatus described above. The joint was sealed at the top half of the ground-glass surface, with the minimum quantity of silicone grease which was consistent with a vacuum-tight joint. The reaction mixture, at atmospheric pressure, was allowed to warm slowly to room temperature as the solid carbon dioxide surrounding the tube volatilised. If no reaction had occurred at room temperature the tube containing the reaction mixture was warmed slowly to 60° in a water-bath, but no higher, as above this temperature perchloric acid slowly decomposes.

Results.—Ferrous and ferric chloride reacted with anhydrous perchloric acid to yield ferric perchlorate dihydrate. Chromous, chromic, manganous, cobaltous, nickelous, and cupric chloride did not react.

Ferrous chloride. No reaction occurred at −80°, but as the mixture warmed to room temperature the initially colourless acid became dark brown and the colourless ferrous chloride was converted into red-brown crystals. During this process the mixture gave off a colourless gas, presumably hydrogen chloride. The reaction mixture was set aside for 12 hr., then cooled in solid carbon dioxide, and the apparatus was evacuated. The excess of perchloric acid was removed by allowing the temperature of the tube to rise slowly to room temperature under a vacuum and then warming it to 60° in a water-bath. Analysis of the red-brown crystals showed them to be ferric perchlorate dihydrate [Found: Fe, 14·12; ClO_4, 74·9; H_2O, 9·5. Calc. for $Fe(ClO_4)_3,2H_2O$: Fe, 14·3; ClO_4, 76·5; H_2O, 9·23%]. No evidence was obtained of any chloride remaining in the solid product.

Ferric chloride. Freshly sublimed ferric chloride was used and transfers were carried out in a dry-box. No reaction occurred at −80°, but on warming to room temperature the initially colourless perchloric acid became dark brown. The mixture was kept for 4—5 days at room temperature; if shorter reaction times were used significant quantities of chloride ion were found in the product. The mixture was then cooled in solid carbon dioxide the apparatus was evacuated, and excess of perchloric acid was removed as above. The product was red-brown; it was not so crystalline as that obtained from the reaction with ferrous chloride, but analysis showed it to be ferric perchlorate dihydrate (Found: Fe, 14·3; ClO_4, 75·0; H_2O, 10·75%).

Discussion.—The above reactions raise three points of interest: (1) Why do only ferrous and ferric chloride react with anhydrous perchloric acid? (2) Why is ferrous chloride oxidised to the ferric state? (3) Why does anhydrous perchloric acid afford the dihydrate and not anhydrous ferric perchlorate?

Because of the unusual features associated with these three points the reactions of the above transition-metal chlorides were examined with anhydrous nitric acid to see if the two acid systems were similar.

Reaction of Anhydrous Transition Metal Chlorides with Anhydrous Nitric Acid.—An excess (4 ml.) of anhydrous nitric acid was pipetted on to ~1 g. of the anhydrous transition-metal chloride at 0° and the mixture allowed to warm slowly to room temperature; reaction then occurred, as indicated by the evolution of hydrogen chloride. The mixture was left overnight, then cooled to −80°, and the excess of nitric acid was removed under a vacuum, as the temperature of the mixture was allowed to rise slowly to room temperature. In the case of manganese, cobalt, nickel, and copper chlorides the product was a crystalline, free-flowing powder; with chromium and iron chlorides the product was soluble in the excess of nitric acid which on evaporation left a viscous gum. The gum required 2—3 days under a vacuum at room temperature, or a shorter period at 60°, for solidification.

The results of these experiments are given in Table 1.

TABLE 1.

			Found (%) *				
Reactant	Rate of initial reaction	Colour of product	Metal	NO_3	H_2O	NO_2	Formulation
$CrCl_2$	Nil	—	—	—	—	—	—
$CrCl_3$	Steady	Violet-grey	19·0	66·3	10·5	—	$Cr(NO_3)_3,2H_2O$
			18·9	67·8	13·1	—	
$MnCl_2$	Rapid	Pale pink	27·8	62·8	10·3	—	$Mn(NO_3)_2,2H_2O$
			27·9	62·9	10·2	—	
$FeCl_2$	Rapid	Red-brown	20·2	71·4	5·8	2·0 ‡	$Fe(NO_3)_3,H_2O$ $0{\cdot}17N_2O_4$
$FeCl_3$	Rapid	Red-brown	19·95	66·5	—	—	$Fe(NO_3)_3,2H_2O$
			20·1	66·9	—	—	
$CoCl_2$	Rapid	Maroon	26·8	56·1	17·3	—	$Co(NO_3)_3,2H_2O$
			26·9	56·7	17·4	—	
$NiCl_2$	Rapid	Leaf-green	26·0	56·9	16·4	—	$Ni(NO_3)_2,2H_2O$
			26·8	56·5	16·7	—	
$CuCl_2$	Slow	Blue †	28·17	55·3	—	—	$Cu(NO_3)_2,2H_2O$
		Green †	31·6	61·8	—	—	$Cu(NO_3)_2,0{\cdot}74H_2O$
$Cu(NO_3)_2$	Nil	Medium blue	29·85	57·0	—	—	$Cu(NO_3)_2,1{\cdot}67H_2O$

* Analysis: the upper figures are the experimental results and the lower figures are the theoretical for the formulations given in the last column.

† Cupric chloride gave a mechanical mixture of blue and green crystals, which were separated by hand for analysis.

‡ The product of the ferrous chloride reaction contained a small amount of combined dinitrogen tetroxide and ferrous ion, but no chloride ion.

Discussion (*contd.*).—The results show that anhydrous nitric acid is much more reactive than anhydrous perchloric acid towards the chlorides examined; thus, while nitric acid reacted with all of them except chromous chloride, perchloric acid reacted only with ferrous and ferric chloride. This may be determined by the solubility of the transition-metal chlorides in the anhydrous acids. In nitric acid reactions the supernatant liquid was always intensely coloured, indicating a significant amount of transition-metal ion in solution. Replacement of the chloride ion by the nitrate ion probably occurs in solution and this explains why the reactions in nitric acid go to completion; this would be helped by preferential removal of the hydrogen chloride liberated, as it is more volatile than nitric acid. In the reaction of ferrous and ferric chloride with perchloric acid the supernatant liquid was dark brown, suggesting a significant solubility of these compounds in this acid. Where no reaction with perchloric acid occurred, the acid remained colourless, indicating a negligible solubility.

As with perchloric acid the products of reaction of anhydrous nitric acid are all hydrated; in general, the mono- or di-hydrate is obtained, whereas from aqueous media a hexahydrate is normally isolated at room temperature. The lower hydrates of these transition-metal nitrates can be obtained by careful dehydration of the hexahydrates, but the product is usually amorphous. The above reactions, therefore, may be considered as useful routes for the preparation of the crystalline lower hydrates.

The reaction of anhydrous copper nitrate with anhydrous nitric acid was carried out to ascertain whether the hydrate was formed during the reaction of the chloride with the nitric acid, or whether the attraction of the copper ion itself is strong enough to abstract water from the anhydrous acid. Since a hydrate is formed in this reaction, it shows that it is the attraction of the transition-metal ion for water which determines the formation of the hydrate as opposed to the anhydrous salt.

The abstraction of water from these acids suggests that both acids are capable of dissociating in such a way as to give rise to free water. In the case of anhydrous nitric acid Dunning and Nutt[1] have suggested that the following equilibria are present in the pure acid:

$$2HNO_3 \rightleftharpoons H_2O + N_2O_5 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$N_2O_5 \rightleftharpoons NO_2 + NO_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^- \quad . \; . \; . \; . \; . \quad (4)$$

Cryoscopic methods[2] have shown the presence of 0·5% of water in the anhydrous acid at $-40°$. The removal of this water by co-ordination to a transition-metal ion will move the equilibrium of equation (2) to the right-hand side, with the corresponding formation of more free dinitrogen pentoxide; this may ionise more extensively, according to equation (3), or alternatively the temporary high concentration of dinitrogen pentoxide may result in decomposition according to equation (5):

$$2N_2O_5 \longrightarrow 4NO_2 + O_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

Evidence suggesting this mode of decomposition is obtained from the observation of nitrogen dioxide in the tube above the reaction mixture during our experiments.

Anhydrous perchloric acid is known to be an equilibrium mixture of the acid, dichlorine heptoxide, and water:[3]

$$2HClO_4 \rightleftharpoons Cl_2O_7 + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

This dissociation has been shown to occur to an extent of 50% even in the freshly distilled acid.[4] If such a large amount of water can be present in the pure acid it is not surprising that the products of reaction of ferrous and ferric chloride with this acid are the hydrated, and not the anhydrous, salts.

According to the above equilibrium both the anhydrous acids contain significant

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[1] Dunning and Nutt, *Trans. Faraday Soc.*, 1951, **47**, 15.

[2] Goddard, Hughes, and Ingold, *J.*, 1950, 2552.

[3] Sidgwick, " The Chemical Elements and Their Compounds," Clarendon Press, Oxford, 1950, Vol. II, p. 1230.

[4] van Wyk, *Z. anorg. Chem.*, 1902, **32**, 115; 1909, **48**, 1.

quantities of reactive oxides, dichlorine heptoxide in the case of perchloric acid and dinitrogen pentoxide in the case of nitric acid. Both of these oxides are strong oxidising agents, so the oxidation of ferrous iron to ferric iron is to be expected in these systems. The failure, in the nitric acid system, to oxidise elements such as manganese, cobalt, and nickel to the known, but less stable, tervalent state may also be associated with the presence of free water in the system, in the presence of which these tervalent ions are known to be unstable.

B. THE REACTION OF ANHYDROUS PERCHLORIC ACID WITH ANHYDROUS METAL NITRATES.

Anhydrous Copper Nitrate.—An excess (5 ml.) of anhydrous perchloric acid, cooled to −80°, was pipetted on to ~2 g. of amorphous anhydrous copper nitrate, contained in a B.24 tube cooled in solid carbon dioxide. The tube was then quickly attached to the apparatus described in the previous section. No visible reaction occurred at −80°, but as the tube was warmed reaction occurred, below 0°. This was indicated by swelling of the copper nitrate powder to twice its volume. The mixture was left at room temperature overnight, but no further reaction occurred. The mixture was then cooled to −80°, the apparatus evacuated, and the excess perchloric acid removed as the temperature was allowed to rise to room temperature; the apparatus was evacuated for 24 hr. at this temperature for complete removal of the perchloric acid. At this stage the product showed an increase of 400% on the original weight of copper nitrate taken. When this product under a vacuum was heated slowly to 100° in a water-bath its weight decreased to ~250% of the original. This was accompanied by formation of a small amount of colourless crystalline sublimate of nitronium perchlorate (Found: ClO_4, 66·5; NO_2, 30·7%; equiv., 72·4. Calc. for $NO_2{\cdot}ClO_4$: ClO_4, 68·4; NO_2, 31·6%; equiv., 72·8). Prolonged heating of the product under a vacuum at 110° was required before constant weight was obtained. The product was pale blue and did not fume in air; this indicated the absence of significant quantities of nitronium perchlorate. A typical analysis gave Cu 24·7, ClO_4 64·2, NO_3 8·2% (total 97·2) [Calc. for $Cu(ClO_4)_2$: Cu, 24·15; ClO_4, 75·85%]. The product was mainly soluble in water, but a small amount of a white insoluble material remained, which may account for the total analysis not adding up to 100%, although the ratio of perchlorate plus nitrate to copper was 2·006. The amount of nitrate is surprisingly high. The above analysis corresponds to a mixed salt $Cu(ClO_4)_{1{\cdot}66}(NO_3)_{0{\cdot}34}$. Reaction of this product with a further quantity of perchloric acid gave a material having the analysis Cu 23·8, ClO_4 66·2, NO_3 5·0 (total 95·0%), corresponding to an empirical formula $Cu(ClO_4)_{1{\cdot}78}(NO_3)_{0{\cdot}22}$, which shows only a slight decrease in the nitrate content. This indicates that preparation of anhydrous copper perchlorate by repeated reaction with perchloric acid is impracticable.

If the mixed copper perchlorate nitrate powder was heated to 140° very little loss in weight occurred as thermal decomposition at this temperature was very slight, but the initially very pale blue powder became a pastel-green and appeared to be more crystalline. Heating this material to 200° under a vacuum resulted in decomposition to a leaf-green basic perchlorate with only a small amount (5%) of sublimation (in contrast to the 80% efficiency of sublimation of the copper perchlorate [5] obtained by the reaction of copper oxide with nitrosyl perchlorate).

Potassium Nitrate.—No visible reaction occurred between potassium nitrate and anhydrous perchloric acid at −80°, or at room temperature, but after 24 hr. in a vacuum at 100° a colourless non-fuming product was obtained. Analysis showed it to be mainly potassium perchlorate (Found: ClO_4, 70·6; NO_3, 2·5. Calc. for $KClO_4$: ClO_4, 71·8%). The high perchlorate and low nitrate figures indicate that the reaction has gone almost to completion with a single application of perchloric acid.

Manganese Nitrate.—No visible reaction occurred between anhydrous manganese nitrate and anhydrous perchloric acid at −80°, or as the mixture was brought to room temperature, but a white powder was obtained after removal of the excess of perchloric acid by evacuation for 24 hr. at 110°. This product still fumed in air but prolonged heating in a vacuum did not completely eliminate it, and in addition it caused partial thermal decomposition to a black basic salt. Analysis of this partially decomposed product showed it to be mainly manganese perchlorate [Found: ClO_4, 59·0; NO_3, 13·5; Mn, 24·4; total 96·9. Calc. for $Mn(ClO_4)_2$: Mn,

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[5] Hathaway, *Proc. Chem. Soc.*, 1957, 19.

21·6; ClO_4, 78·4%]. The high nitrate figure shows that only about 75% of the nitrate has been converted into perchlorate, which is significantly less than the 85% conversion with copper nitrate. The low perchlorate figure and high manganese figure occur through thermal decomposition of the initial perchlorate formed to a basic perchlorate.

Discussion.—These results show that anhydrous perchloric acid will react with anhydrous nitrates to yield the corresponding perchlorate, but only in the case of a simple ionic nitrate, such as potassium nitrate, is reaction complete. With nitrates, such as copper and manganese, which have some degree of covalent character, the reaction is only 80—90% complete. The initial reaction may be represented:

$$KNO_3 + HClO_4 \longrightarrow KClO_4 + HNO_3 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The nitric acid liberated in this reaction is present in excess of perchloric acid; in this medium Goddard, Hughes, and Ingold[2] have shown that it reacts according to the equation:

$$HNO_3 + 2HClO_4 \rightleftharpoons H_3O^+ClO_4^- + NO_2^+ClO_4^- \quad . \quad . \quad . \quad . \quad (8)$$

Therefore the complete reaction of perchloric acid with the above nitrates should be represented:

$$KNO_3 + 3HClO_4 \longrightarrow KClO_4 + H_3O{\cdot}ClO_4 + NO_2{\cdot}ClO_4 \quad . \quad . \quad (10)$$

$$Cu(NO_3)_2 + 6HClO_4 \longrightarrow Cu(ClO_4)_2 + 2H_3O{\cdot}ClO_4 + 2NO_2{\cdot}ClO_4 \quad . \quad (11)$$

Both nitronium and hydroxonium perchlorate are colourless solids at room temperature, so that in the copper nitrate reaction there should be a theoretical increase in weight, after reaction, of 422%. Experimental increases in weight of up to 400% have been obtained for this reaction, but it is difficult to be certain that all the excess of perchloric acid has been removed (both perchloric acid and nitronium perchlorate fume in air so that it is impossible to check for complete removal of the former by fuming of the product). In addition, loss of hydroxonium perchlorate occurs at temperatures only slightly above room temperature; therefore raising the temperature to ensure complete removal of the perchloric acid results in some loss of hydroxonium perchlorate. This difficulty, combined with the uncertainty of a complete reaction, makes it understandable that the theoretical increase in weight of 422% was not attained in practice.

As the temperature of the product was raised to 100°, while under a vacuum, more extensive decomposition of hydroxonium perchlorate occurred. The nitronium perchlorate was much more stable, but thermal decomposition was significant at 110°, although 24 hr. under vacuum was required for its complete removal. The isolation of a small quantity of nitronium perchlorate, as a crystalline sublimate at 100°, was the only evidence obtained that the nitric acid liberated according to equation (8) was converted into a mixture of nitronium and hydroxonium perchlorate. No analytical evidence of the formation of hydroxonium perchlorate has been obtained, but the isolation of nitronium perchlorate requires its formation according to equation (8). Isolation of a crystalline sublimate of nitronium perchlorate is the first indication that it can be sublimed and, therefore, that it can possibly exist in the vapour phase as a distinct molecule with some degree of covalent bonding between the nitronium ion and the perchlorate ion. Alternatively a Referee has pointed out that the sublimation may be explained by a dissociation process such as $2NO_2{\cdot}ClO_4 \longrightarrow N_2O_5 + Cl_2O_7$.

The use of a temperature of 110° for the removal of the nitronium perchlorate was a compromise between the removal of the latter as quickly as possible and working at as low a temperature as possible to prevent thermal decomposition of the product to a basic salt, which occurred above 120° and the formation of which was indicated by insolubility of the product in water.

The product of the reaction between anhydrous copper nitrate and anhydrous perchloric acid has been shown to be a mixed copper perchlorate nitrate, which contains only a small amount of nitrate, but in all cases the analytical figures were 3—5% low on 100%. This factor by itself does not justify considering the product other than as an anhydrous copper salt, but when combined with the observation that the product could be sublimed only with a very low efficiency it suggests that the product was not an anhydrous salt, but a hydrated one. If it is hydrated, heating under a vacuum at 100° would result in decomposition to a basic salt, with only a slight amount of sublimation.

The infrared spectra of the above copper perchlorate nitrate was measured and strong peaks were found at 1154, 1025, and 930 cm.$^{-1}$, which are associated with a covalently bonded perchlorate ion,[6] but in addition strong adsorption was obtained at 1622 cm.$^{-1}$, which corresponds very closely with the O–H stretching frequency of 1628 cm.$^{-1}$ of hydrated copper perchlorate.

These three lines of evidence suggest strongly that the product obtained is not the anhydrous salt but a partially hydrated material. This shows that copper perchlorate is able to abstract water from anhydrous perchloric acid in the same way as ferric perchlorate does, as described in section A of this paper.

Conclusions.—From the results of sections A and B of this paper it is concluded that anhydrous perchloric and nitric acid react with various transition-metal salts as though they are equilibrium mixtures of the free acid, the acid anhydride, and water:

$$2HClO_4 \rightleftharpoons Cl_2O_7 + H_2O$$
$$2HNO_3 \rightleftharpoons N_2O_5 + H_2O$$

Owing to the strong affinity of transition-metal ions for water, that liberated in the above reactions can be removed as the hydrated salt. For this reason neither anhydrous perchloric acid nor anhydrous nitric acid can be used as reagents for the preparation of anhydrous transition-metal perchlorates or nitrates.

EXPERIMENTAL

Anhydrous perchloric acid was prepared by Smith's method,[7] except that all ground-glass joints were sealed with a minimum quantity of silicone grease instead of 72% aqueous perchloric acid; use of the latter resulted in very low yields of perchloric acid as the joints failed to hold a vacuum. The preparation was always carried out on a small scale, producing 4—5 ml. of the acid per run; preparation and manipulation of the anhydrous acid were carried out behind blast-screens.

A frequent occurrence during the work described in this paper was the necessity to destroy excess of perchloric acid contaminated with oxides of chlorine. This was at first carried out by pouring the liquid into an excess of water, as perchloric acid is a strong acid, but as this involved the liquid passing over the greased joint at the mouth of the tube, there were frequent explosions. To avoid this, water was added dropwise to the liquid, at −80°; this procedure was safe so long as the water was added slowly.

Anhydrous nitric acid was prepared by low-temperature distillation, under reduced pressure, of a 3 : 1 mixture of concentrated sulphuric acid and 70% nitric acid. The purity of the acid was checked by analysis.

The anhydrous transition-metal chlorides were obtained by standard procedures.[8]

Anhydrous manganese nitrate was prepared [9] by treating manganese with dinitrogen tetroxide and ethyl acetate for 24 hr. Excess of dinitrogen tetroxide was added to the resultant viscous solution, and the manganese nitrate–dinitrogen tetroxide addition compound, which was precipitated, was filtered off. The addition compound was decomposed by heating it under a vacuum for 24 hr. at 90°; this left the anhydrous manganese nitrate as an off-white powder.

Analysis for metal ions was carried out by standard methods; [10] nitrate was estimated by a

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[6] Hathaway, unpublished work.

[7] Smith, *J. Amer. Chem. Soc.*, 1953, **75**, 184.

[8] *Inorg. Synth.*, Vols. I—V.

[9] Addison and Hathaway, unpublished work.

[10] Vogel, " Text Book of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 2nd edn., 1951.

micro-Kjeldahl technique, nitrite by addition of excess of potassium permanganate and back-titration with standard ferrous ammonium sulphate, and combined nitrate and perchlorate gravimetrically by nitron reagent.

The authors are indebted to the Department of Scientific and Industrial Research for a Maintenance Grant (to A. E. U.).

THE CHEMISTRY DEPARTMENT, THE UNIVERSITY, HULL. [*Received, August 10th,* 1959.]