A METHOD for the PREPARATION OF PERCHLORIC ACID

Thesis

by

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I. Purpose.

Perchloric Acid is a substance resembling sulfuric acid in many respects. It is a strong acid, very stable in solution, and has a high boiling point. It possesses some advantages over sulfuric acid, such as being monobasic, and having relatively few insoluble salts. (K, Rb, Cs, and Tl perchlorates are only slightly soluble.) Hence a cheap way of making perchloric acid would be highly advantageous to the chemical industry. The present methods of its production are rather expensive, employing the electrolytic production of sodium perchlorate and the distillation of the latter with sulfuric acid under reduced pressure. The product, a 60% perchloric acid is now sold for $7 to $8 per pound. Ammonium perchlorate is obtainable at a fairly low cost, (about 20¢ per pound) and might be used as a basis for the cheaper preparation of perchloric acid.

Obviously the most direct method of accomplishing this would be the replacement of the NH_4 radical in NH_4ClO_4 by H. It is proposed in this paper to find whether the ammonium ion in ammonium perchlorate solution can be oxidized by means of the oxides of nitrogen, producing only perchloric acid solution and gaseous products. The ideal reaction would be:

(I) $2NH_4ClO_4 + N_2O_3 = 2N_2 + 2HClO_4 + 3H_2O$

This leaves no reaction products from which the perchloric acid need be purified, and hence it is desired to approach in practice this equation as closely as possible.

II. Previous Work.

Only few results on the oxidation of NH_4^+ ion by nitrous fumes have been published. Besson and Rosset* tried the action of NO_2 on ammonia and ammonium salts, and found, for example, the reaction to take place as follows:

$$(NH_4)_2SO_4 + 4NO_2 = 2N_2 + 2HNO_3 + H_2SO_4 + 2H_2O$$

This reaction they found to be greatly accelerated when the solution was heated to 100° C.

H.H. Willard** produced perchloric acid from ammonium perchlorate by dropping hydrochloric acid on a mixture of nitric acid and ammonium perchlorate. In this reaction, the hydrochloric acid probably

*Compt. Rend. 142, (1906) 633.
**J. Am. Chem. Soc. 34, (1912) 1480-85.

reduced the nitric acid, forming among other products HNO_2, which latter acted upon the ammonium perchlorate in the manner shown by Equation I above. He actually reports the reaction to be as follows:

$$34NH_4ClO_4 + 36HNO_3 + 8HCl = 34HClO_4 + 4Cl_2 + 35N_2O + 3H_2O$$

This he obtained empirically from analysis during the reaction. That the conversion was not due to the oxidizing action of the chlorine formed, he showed by passing chlorine thru a solution of ammonium perchlorate and finding no change. He concludes that the nitrous acid formed by the reduction of nitric acid must have been the active oxidizing agent in the reaction.

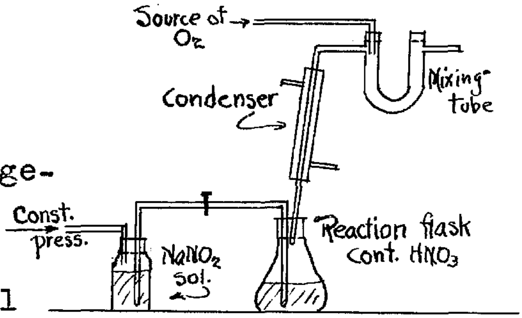
It would seem, therefore, that nitrous acid alone might be made to act on ammonium perchlorate, the final solution containing only perchloric acid. To this end, N_2O_3, the anhydride of HNO_2 might be employed.

III. Experimental.

a) The gases.

The preparation of nitrous gases in the laboratory is most conveniently carried out by the reduction of nitric acid. Lunge[*] found that it was possible to obtain a gas of varying composition by the reduction of nitric acid with starch or As_2O_3, the proportion of NO_2[**] to NO depending upon the concentration of the acid. This method does not, however, afford a conveniently controlable supply of the gas. The method used in this laboratory was as follows:

A nearly saturated solution of sodium nitrite (840 grams per liter) was forced under constant pressure into a flask containing nitric acid. The reaction between sodium nitrite and nitric acid is almost instantaneous, forming a mixture of NO and NO_2. The gas was run thru a tap water condenser (B.P. of NO_2 = 22°) to condense water or nitric acid being carried over with the gas. This arrangement gave a steady source of gas at pressures up to several feet of water. The composition of the gas varied, the proportion of NO becoming greater as the acid was



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[*] Ber. 11, 1229 and 1641.

[**] At room temperatures, NO_2 is of course mostly in the form of its polymer, N_2O_4. Because of its simplicity, the formula NO_2 will be used thruout this paper with these polymeric properties in mind.

diluted by the sodium nitrite solution.

For the analysis of the gas, various absorption methods were tried. In one method a series of two glass-tube coils containing respectively NaOH and acidified $KMnO_4$ solution was used, the gas bubbling thru the apparatus. Another method employed the use of two beakers containing the absorption liquids, the gas being sprayed thru the solutions to get intimate contact. In both these bubbling methods, the absorption was found to be incomplete with single units, while the addition of more units to insure completeness was not feasible because of uneveness of flow and surging, due to the back pressure created. The most reliable analyses were found to be obtained by filling a closed flask with the gas, introducing the absorbing solution and shaking. Since NO_2 is brown, and NO colorless, it is possible to determine the completeness of absorption of NO_2 by the absence of color. The analysis as actually performed follows:

A 350 cc round bottom flask was completely filled with carbon tetrachloride vapor (by boiling CCl_4 in the flask) and then attached to the gas generator. As the vapor condensed, gas was drawn in. When cooled to room temperature, the flask was disconnected. 8-10 cc of 2N NaOH (diluted to about 50 cc) were then introduced and the flask well shaken. All the brown NO_2 fumes disappeared in a very short time. The alkaline solution was drawn off and titrated with sulfuric acid for unused alkali, then with $KMnO_4$ for nitrite. To find the amount of unabsorbed NO left in the flask, 50 cc of acidified .1m $KMnO_4$ were introduced, and the flask again well shaken. The resulting solution was titrated with ferrous ammonium sulfate for unused permanganate. The reactions in the separate steps are assumed to be as follows:

$$1)\ \begin{cases} 2NO_2 + 2NaOH = NaNO_3 + H_2O + NaNO_2 \\ NO_2 + NO + 2NaOH = 2NaNO_2 + H_2O \end{cases}$$

$$2)\ 5NaNO_2 + 2KMnO_4 + 6H^+ = 5NaNO_3 + 2K^+ + 2Mn^{++} + 3H_2O$$

$$3)\ 5NO + 3KMnO_4 + 9H^+ = 3K^+ + 3Mn^{++} + 5HNO_3 + 2H_2O$$

With the aid of these equations it can be shown that if

A = mols NaOH neutralized (Eq. 1.)

B = mols $KMnO_4$ used to oxidize nitrite (Eq. 2)

C = mols $KMnO_4$ used to oxidize NO undissolved in NaOH (Eq. 3.)

then the composition of the gas is as follows:

Mols of NO = $(5B - A)/2 + 5C/3$ and

Mols of NO_2 = $(3A - 5B)/2$

The assumption is here made that there are no other gases but these in the mixture.

A typical analysis performed in this manner gave the following composition of a gas generated with fresh nitric acid and nitrite solution:

A = .0137 mols NaOH

B = .00292 mols $KMnO_4$

C = .00078 mols $KMnO_4$

So that

NO = .00175 mols and NO_2 = .0132 mols.

The amount of NO that had dissolved with the NO_2 in the sodium hydroxide was in this case only .00045 mols, as compared with .0132 mols of NO_2. This shows that the gases in the mixture retain their properties individually at least as far as this reaction is concerned, so that an equal molal mixture of NO and NO_2, corresponding to the composition N_2O_3 has but little tendency to behave as a compound N_2O_3. For this reason the gas used in some of the tests given later on was made as large in NO_2 content as possible by the introduction of oxygen into the generator gas. The reaction

$$2NO + O_2 = 2NO_2$$

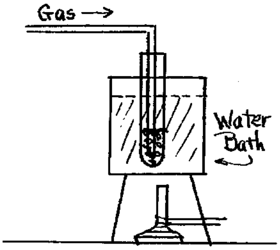
is very rapid at room temperature.

b) Actual Tests.

The ammonium perchlorate sample used in the following runs was obtained from the Atlas Powder Co., and contained about 98% NH_4ClO_4. This was recrystallized and dried, thus removing a small quantity of iron impurities. Its solubility is about

89 g per 100 g water at 100°C and
13 g per 100 g water at 0°C.

The apparatus used was simply a 9" test tube, containing a solution of 5 g NH_4ClO_4 in 20 g water, glass beads to the surface of the liquid, and a piece of glass tubing drawn down at one end to break up the gas into fine bubbles, and run to the bottom of the test tube. This tube was connected to the gas apparatus. The nitrous fumes were passed thru the solution fairly rapidly, not all the gas being absorbed. A water bath surrounded the whole reaction tube so that a constant temperature could be maintained. At the end of the run the solution was analyzed for total acidity with 2N NaOH, then the whole made strongly alkaline and distilled in a Kjeldahl apparatus, the unconverted ammonium perchlorate liberating NH_3, the latter being absorbed in a flask containing .5N sulfuric acid. These determinations give a basis for the calculation of the amount of perchlorate converted to the acid. Various factors, such as the time of passage of the gas, concentration of acid, and temperature, were changed for different runs. The tabulated results for some of the runs follow:



No.	Character of sol.	Character of gas	Total acid	Time	NH_3 content at end	%Conv.
1	Neutral, Hot	NO_2	.118 eq.	1/2hr	.0098 eq.	77%
2	" "	"	.098	1/2	.0069	84
3	" "	"	.180	1	.00045	99
4	Neutral, Cold	"	.149	1/2	.04 +	<6
5	Conc. HNO_3 Hot	"		25 min.		very small

Five grams of NH_4ClO_4 correspond to .0426 equivalents, and the per cent. conversion is based on this figure. It is to be noted that in these runs the gas used was simply generator gas which had been converted by an excess of oxygen entirely into NO_2. This was done for economy of gas, because there was evidence that when generator gas alone was used, a large part of it was wasted, due to the inactivity of the NO, the latter passing thru the solution with little or no action. In all runs except the last, (No.5), the solution at the start consisted simply of ammonium perchlorate dissolved in water. No. 5 was a solution of the salt in concentrated nitric acid (Sp.Gr. 1.42). All except No. 4 were run at a temperature near the boiling point of water. Run No. 2 was similar to No. 1, except that the gas was passed thru only rapidly enough so that there was only slight loss because of non-absorption, i.e. the gas above the solution was not markedly colored. The conclusions to be drawn from these experiments may be summarized as follows:

1. Increased temperature has a marked effect in accelerating the reaction,
2. The action is much slower at high acid concentrations, and
3. Practically complete conversion may be attained at 100° C if the gas is passed thru a sufficiently long time. Also
4. Altho no quantitative results on this question were obtained, it could readily be seen during the course of the experiment that a gas rich in NO (shown by light color)

was much less absorbed by the solution than an NO_2-rich mixture. In the above case, the gas coming from the solution was almost colorless, but browned considerably on coming in contact with the air. Hence NO is probably quite ineffective in the conversion of ammonium perchlorate. For most efficient absorption, then, pure NO_2 is most desirable.

This inactivity of NO is of course somewhat disadvantageous, because when NO_2 alone is used, the formation of perchloric acid will be accompanied by the simultaneous formation of nitric acid in equi-molal quantities. The mechanism of the reaction might be thought of as follows:

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

$$HNO_2 + NH_4ClO_4 = HClO_4 + N_2 + 2H_2O$$

For the preparation of pure NH_4ClO_4 it will thus be necessary to distil off the nitric acid thus formed in the reaction. However, since commercially it would be necessary to concentrate the acid anyway, the nitric acid would be automatically distilled off in the concentration process.

It is of course conceivable that if a gas corresponding to the composition N_2O_3 were formed directly in the reaction tube in the presence of the ammonium perchlorate, it would act more efficiently, for that is practically what happens when NO_2 is dissolved in the solution.

In preparing the gases commercially, it would be more economical to obtain them by the catalytic oxidation of ammonia than to reduce nitric acid, as was done in these experiments.

For the suggestion of the problem and its possible solution, and for the numerous helpful suggestions, acknowledgment is here made to Dr. A.A. Noyes, Director of Chemical Research, this institute.

IV. Summary.

1. It has been shown that the reaction

$$N_2O_3 + 2NH_4ClO_4 = 2N_2 + 2HClO_4 + 3H_2O$$

is impracticable because of the fact that a gas corresponding to the composition N_2O_3 acts as a mixture of NO_2 and NO, in which the NO is much less active than the NO_2, Passing thru the solution with little or no action.

2. It would be more economical of gas to use the

reaction

$$2NO_2 + NH_4ClO_4 = N_2 + HClO_4 + HNO_3 + H_2O$$

This of course involves the distillation of nitric acid from the product, which however occurs simultaneously with the concentration of the product.

3. At 100° C, ammonium perchlorate may be practically completely converted to perchloric acid by means of NO_2 gas.