[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Preparation of Ammonium Trinitride from Dry Mixtures of Sodium Trinitride and an Ammonium Salt

BY W. J. FRIERSON AND A. W. BROWNE

Ammonium trinitride may be prepared in the pure state by the metathetical reaction between sodium trinitride and an ammonium salt such as the sulfate or the nitrate

$$NaN_3 + (NH_4)_2SO_4 \longrightarrow NH_4N_3 + NaHSO_4 + NH_3 \qquad (I)$$

$$NaN_3 + NH_4NO_3 \longrightarrow NH_4N_3 + NaNO_3 \qquad (II)$$

Equimolecular mixtures of the dry reagents were heated either statically in a sealed tube, *in vacuo*, or dynamically in a simple sublimation apparatus through which was passed a continuous current of dry air.

Mixtures containing 1 g. of ammonium sulfate and 0.4924 g. of sodium trinitride repeatedly were found to yield 87% of the theoretical amount of ammonium trinitride when heated to 300° for forty-five minutes in the current of air. The amounts of free ammonia were found to correspond closely to the theory based upon Equation I. Because of the relatively low melting point of ammonium nitrate, mixtures containing one gram of this reagent with 0.8125 g. of sodium trinitride gave consistent yields of over 93% of the volatile salt when heated to 190° for thirty minutes. In a series of experiments with the nitrate mixtures *in vacuo* a maximum yield of 95.7% was obtained after a five-hour period at 190°. The dynamic method with ammonium nitrate was adjudged most satisfactory, in view of the lower temperature and the shorter time required.

The white, crystalline sublimate was shown by the standard qualitative tests,[1] and by quantitative analysis involving repeated determinations of both ammonia and the trinitride ion, to be ammonium trinitride of a high degree of purity. Experiments with mixtures of the reagents in other than equimolecular proportions led to no improvement in the yields of ammonium trinitride.

Failure to obtain strictly quantitative yields is in no case attributable to loss of the N_3 radical by decomposition, but rather to the difficulty of securing satisfactory contact between the reagents. In a number of experiments the amounts of N_3 left in the reacting mass have been determined, with the result that it was found possible to account for over 99% of the trinitride originally taken.

In the opinion of the authors the reaction between sodium trinitride and an ammonium salt, or a suitable eutectic mixture of two or more ammonium salts, might readily be adapted for use on a larger scale, with certain precautions to minimize danger of detonation.

(1) Browne, THIS JOURNAL, **27**, 551 (1905).

ITHACA, N. Y. RECEIVED SEPTEMBER 5, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Further Studies of the Oxides of Potassium

BY CHARLES A. KRAUS AND ELLIS F. PARMENTER[1]

Of the various oxides of potassium reported in the literature, only K_2O, K_2O_2, K_2O_3 and K_2O_4 seem actually to exist. Of these, K_2O_4 has been established definitely by Vernon-Harcourt[2] and Holt and Sims[3] and has been confirmed by Kraus and Whyte.[4] Holt and Sims report a buff-colored oxide, K_2O_3, but without analytical details. They also report a yellow product whose oxygen content corresponded roughly to that of K_2O_2, but Kraus and Whyte report K_2O_2 as white.

Rengade[5] reports an oxide, K_2O, but its behavior toward liquid ammonia indicates that it may have been impure. While Kraus and Whyte obtained K_2O_2 and K_2O_4 by oxidation of potassium in liquid ammonia, they could obtain no evidence of the formation of an intermediate oxide, K_2O_3.

In the present investigation K_2O_2 and K_2O_4

(1) Du Pont Fellow in Chemistry at Brown University.

(2) Vernon-Harcourt, *J. Chem. Soc.*, **14**, 267 (1861).

(3) Holt and Sims, *ibid.*, **65**, 432 (1894).

(4) Kraus and Whyte, THIS JOURNAL, **48**, 1781 (1926). The earlier literature is reviewed by these authors.

(5) Rengade, *Ann. chim. phys.*, [8] **11**, 348 (1907).

have been prepared in a higher degree of purity by oxidation of potassium in liquid ammonia. The interaction of K_2O_2 with oxygen has been studied and the behavior of the oxides K_2O_2, K_2O_3 and K_2O_4 toward water has been investigated. The existence of the hydrates $K_2O_2 \cdot H_2O$, $K_2O_2 \cdot 2H_2O$ and $K_2O_3 \cdot H_2O$ has been established and some of their properties have been investigated.

I. Method

The apparatus employed was similar to that of Kraus and Whyte but with numerous variations in detail, a description of which is omitted for the sake of brevity. Means were provided for measuring oxygen absorbed in the oxidation process or evolved when the various oxides were treated with water. The samples of potassium used were filled into weighed, fragile glass bulbs and introduced into a weighed reaction tube of the type described by Kraus and Whyte.

The products dealt with in the present paper do not admit of purification, for which reason it was necessary to obtain starting materials of the highest possible purity. The weight of the product formed upon oxidation of potassium in liquid ammonia is not a satisfactory criterion of purity of K_2O_2 or K_2O_4 because of the formation of K_2O which ammonolyzes to KOH and KNH_2, the latter compound being readily oxidizable.

In order to determine the nature of the reaction product, it was treated with water. With liquid water at 0°, K_2O_4 reacts according to the equation

$$K_2O_4 + aq = K_2O_2 \cdot aq + O_2 \qquad (1)$$

as shown by Holt and Sims.[3] We have found that the oxide K_2O_3 reacts similarly according to the equation

$$K_2O_3 + aq = K_2O_2 \cdot aq. + {}^1/_2O_2 \qquad (2)$$

while K_2O_2 dissolves in ice-cold water without evolution of oxygen. The aqueous solution of K_2O_2 decomposes at higher temperature according to the equation

$$K_2O_2 \cdot aq = KOH \cdot aq. + {}^1/_2O_2 \qquad (3)$$

On treating K_2O_4 with water vapor, reaction takes place according to the equation

$$K_2O_4 + 3H_2O = K_2O \cdot 3H_2O + {}^3/_2O_2 \qquad (4)$$

The amount of oxygen evolved in the course of the reaction is practically equivalent to the water vapor introduced, although frequently a trifle less.

The above reactions have enabled us to determine the nature of the reaction products. The water is preferably added in liquid ammonia solution, in which case no oxygen is evolved until the liquid has been evaporated and the atmosphere of ammonia vapor exhausted. The oxygen evolved on treating the higher oxides with ice water, referred to as "stage 1" below, serves to determine the amount of oxygen combined in excess of K_2O_2. The oxygen evolved on heating the resulting solutions, referred to as "stage 2," is a measure of the total amount of potassium present in the form of oxides, K_2O_2, K_2O_3 or K_2O_4.

II. Potassium Tetroxide

Preparation in Liquid Ammonia.—The oxide prepared by rapid oxidation of potassium in liquid ammonia by the method of Kraus and Whyte yields a product whose weight corresponds closely to that of K_2O_4. Analysis of the product by means of reactions (1) and (3) indicates the presence of considerable impurities, probably KOH and KNO_2, the latter compound resulting from the oxidation of KNH_2. By oxidizing potassium at −50°, a product may be obtained of 99% purity or better. Analyses of several samples according to reactions (1) and (3) are given in the following table.

TABLE I

ANALYSES OF K_2O_4

K_2 (m.m.)	O abs. (by wt.)	O/K_2 (wt.)	O, stages 1 + 2	O/K_2 (evolved)	% K_2O_4
3.51	14.16	4.03	10.48	2.99	99.4
4.92	19.61	3.99	14.65	2.98	99.2

The results above indicate, on the one hand, the purity of the K_2O_4 and, on the other, confirm reactions (1) and (3) which were not actually separated in the present case.

Direct Oxidation of Potassium.—A single sample of potassium was successfully oxidized at room temperature over a period of some six weeks. Metallic potassium was dissolved in liquid ammonia which was rapidly evaporated so as to spread out the potassium in a thin film over the surface of a tube of 300 cc. capacity. Oxygen was initially introduced at several millimeters pressure and later up to atmospheric pressure until all free metal had disappeared. The final product was of cream color. The following data confirm the formation of K_2O_4: K_2, 1.92; O abs., 7.71; O/K_2, 4.01.

Numerous other samples were prepared and treated with oxygen in similar manner but, while oxidation occurred in all cases, the reaction did not go to completion even at the end of a year. The colors, too, varied greatly in the case of different samples, being, in various instances, cream, brown, cinnamon and yellow. In most cases, the tube was of mottled appearance but in two samples the product had a uniform cinnamon color.

Action of Water Vapor.—With water vapor, K_2O_4 reacts according to equation (4), one atom of oxygen being evolved per mole of water. Once the breakdown of the K_2O_4 has been initiated, it decomposes completely to potassium hydroxide, while the remaining K_2O_4 remains intact. This is indicated by the fact that on incomplete decomposition of K_2O_4, the oxygen evolved in stage 2 is one-half that of stage 1. This is illustrated by the following data: K_2, 3.20; O abs. (wt.), 12.68; H_2O, 6.06; O evolved, 5.28; O stage 1, 2.52; O stage 2, 1.06; total O evolved, 8.86. The sample was impure, containing 2.95 moles of K_2O_4 as indicated by the total O evolved. 1.76 m. moles of K_2O_4 broke down according to equation (4) and the remaining 1.19 m. moles of K_2O_4 yielded a total of 3.58 m. atoms of oxygen as against 3.57 required for K_2O_4 in stages 1 and 2, the amount evolved in stage 1 being slightly greater than twice that of stage 2.

Action of Water in Liquid Ammonia.—Water added to K_2O_4 suspended in liquid ammonia shows no indication of reaction so long as liquid ammonia or ammonia vapor is present. On exhausting the tube at −30°, about three-fifths of the oxygen equivalent to the water added is evolved and the remainder is evolved as the product warms to 25°. On decomposing the residual product with water, the oxygen evolved in stage 1 is twice that in stage 2. The data follow: K_2, 3.51; O abs. (wt.), 14.16; H_2O, 6.91; O evolved at −30°, 3.65; O evolved at 25°, 3.06; total O, 6.71; O stage 1, 2.51; O stage 2, 1.26; total O, 10.48; $3 \times K_2$, 10.53. According to the data, 6.71 atoms of oxygen were evolved on addition of 6.91 moles of water. Decomposition occurred according to equation (4); the residual product was evidently K_2O_4, since the oxygen evolved in stages 1 and 2 is in the ratio of 2:1. The initial material was of 99.5% purity as indicated by the total volume of oxygen evolved.

III. Potassium Dioxide, K_2O_2

Preparation and Properties.—This oxide is best prepared by passing oxygen through a solution of potassium in liquid ammonia at temperatures between −50 and −60° until the color due to free metal disappears. Lower temperatures are not practicable because the colloidal solution of K_2O_2 becomes extremely viscous while, at higher temperatures, measurable quantities of K_2O_2 are reduced to K_2O which, in turn, ammonolyzes to KOH and KNH_2. It is possible to obtain a product having a purity of 99%. The weight of the product is not a safe indication of the purity of the material because of the ammonolysis of K_2O and possible oxidation of the resulting KNH_2. Ammonia is strongly absorbed by K_2O_2 and is given off with difficulty even at 100°. Preparations at −33° rarely have a purity in excess of 90%.

Potassium dioxide exhibits a white to cream color in liquid ammonia or in the presence of ammonia vapor. When the atmosphere of ammonia is removed at room temperature or lower, the color becomes light yellow and this color change is reversible. On removing completely the ammonia by prolonged heating in a vacuum at 100°, the oxide assumes an olive-brown color. Potassium dioxide reacts violently with oxygen at pressures as low as 1 cm. At lower pressures, it forms first an intermediate oxide, K_2O_3, and finally the tetroxide, K_2O_4, which cannot be oxidized further.

Action of Water Vapor.—Potassium dioxide absorbs water vapor, without evolution of oxygen, to form a monohydrate and a dihydrate. The latter compound, in the presence of excess water vapor, loses approximately one atom of oxygen per mole of water according to the equation

$$K_2O_2 \cdot 2H_2O + H_2O = K_2O \cdot 3H_2O + {}^1/_2O_2 \qquad (5)$$

Water vapor was allowed to react with a sample of K_2O_2 at 25° until oxygen began to appear, when successive known portions of water vapor were added and the evolved oxygen for each portion determined. The data follow: K_2, 4.14; initial H_2O added, 8.61; O evolved, 0.13; additional H_2O, 2.33, 2.92, 3.87; O evolved, 2.28, 3.13, 3.84; ratio O/H_2O 0.98, 1.07, 0.99; total O, 3.97; K_2O_2 present, 3.97; % purity 96.

IV. Potassium Trioxide, K_2O_3

Preparation.—On allowing oxygen to react with K_2O_2 at room temperature at low pressures, the light cream color of the dioxide gradually darkens and becomes a chocolate brown, which fades and finally becomes light yellow as the oxide is converted to K_2O_4. At room temperature, oxidation is rapid, particularly in the first stage; oxidation proceeds rapidly even at −33°. Since only the color of the oxide can be used as an indicator of the completeness of oxidation, it is not possible to prepare a compound of absolute purity. Its existence in the presence of K_2O_2 is readily demonstrated by the ratio of oxygen evolved in stages 1 and 2. The data follow: K_2, 3.65; O stage 1, 2.88; O stage 2, 3.49; % K_2O_2, original sample, 96.5.

Of the 3.65 moles of K_2, 3.49 moles, or 96.5%, were converted to K_2O_2 and 2.88 moles of this K_2O_2, or 81%, were converted to K_2O_3. The K_2O_3 lost its oxygen on treatment with liquid water according to equation (2).

Action of Water Vapor.—K_2O_3 absorbs one mole of water vapor at room temperature with the formation of a hydrate and without evolution of oxygen. In the preparation, the chocolate color of the oxide gives way to yellow. On further addition of water vapor, one atom of oxygen is evolved per mole of water added. If less than one mole of water is added, per mole of K_2O_3, the remainder of the oxide may be oxidized to K_2O_4. The data for several experiments follow: K_2, 3.05, 3.36; O absorbed at K_2O_3 stage, 8.51, 9.59; H_2O added, 1.33, 1.82; O absorbed after hydration, 2.29, 1.93; total O + H_2O absorbed, 12.52, 13.35; $4 \times K_2$, 12.20, 13.44.

The sum of oxygen and water per mole of K_2 is equal to $4K_2$; K_2O_3 that has been hydrated does not absorb oxygen. As is shown below, potassium trioxide monohydrate, $K_2O_3 \cdot H_2O$, may also be prepared by oxidizing potassium dioxide monohydrate, $K_2O_2 \cdot H_2O$.

V. Hydrates of the Oxides of Potassium

While, as shown above, K_2O_2 and K_2O_3 absorb definite quantities of water vapor without evolution of oxygen, this method of preparation of the hydrates is not a satisfactory one because of the tendency of the hydrates to rearrange to K_2O_4 and $K_2O \cdot H_2O$ at ordinary temperatures. The hydrates are best prepared by introducing the necessary quantity of water into a suspension of the oxides in liquid ammonia.

Potassium Dioxide Monohydrate, $K_2O_2 \cdot H_2O$.—On treating a suspension of K_2O_2 in liquid ammonia with water, the cream color of the suspension gives way to a dark brown color which is characteristic of the monohydrate. Further addition of water yields a dihydrate which is white. Hydration evidently takes place in liquid ammonia. The monohydrate is of light pink color when completely free from ammonia.

A sample of K_2O_2 was treated with one mole of water and the resulting product, after evaporation of the ammonia, was decomposed with liquid water. Results follow: K_2O_2, 4.18; H_2O added to NH_3, 4.14; O stage 1, 0.18; O stage 2, 3.96; total O, 4.14. As may be seen, practically all of the oxygen was evolved in stage 2, indicating the absence of higher oxides. The slight evolution of oxygen in stage 1 was probably due to rearrangement of the monohydrate, equation (6) below. The K_2O_2 was of 99% purity.

Potassium dioxide monohydrate may be oxidized to potassium trioxide monohydrate at room temperatures. A sample of $K_2O_2 \cdot H_2O$ was prepared and the ammonia removed at −25° in order to prevent the rearrangement of the hydrate to K_2O_4. Oxygen was rapidly absorbed at room temperature, the pink color of $K_2O_2 \cdot H_2O$ giving way to the cream color of $K_2O_3 \cdot H_2O$. The data follow: K_2, 4.36; H_2O added to NH_3, 4.12; O absorbed at 25° (vol.), 3.75; O stage 1, 4.69; O stage 2, 4.13. The slight excess of oxygen in stage 1 over stage 2 was doubtless due to the presence of a small amount, 0.28 m. mole, of K_2O_4 which probably resulted from rearrangement of the trioxide, equation (8) below. The amount of oxygen evolved in stages 1 and 2 indicates the presence of 3.85 moles of $K_2O_3 \cdot H_2O$ and is in good agreement with 3.75 atoms of oxygen absorbed.

Potassium Dioxide Dihydrate, $K_2O_2 \cdot 2H_2O$.—When K_2O_2 is treated with water in liquid ammonia, no oxygen is evolved until two moles of water have been absorbed per mole of K_2O_2. Decomposition of the resulting product shows that the dioxide has been hydrated. The data follow: K_2, 5.05, H_2O in NH_3, 9.53; O stage 1, 0.13; O stage 2, 4.69.

Practically no oxygen was evolved in stage 1 while the oxygen evolved in stage 2 corresponds to 92.8% for the total potassium. Had a higher oxide been present, larger quantities of oxygen must have been evolved in stage 1. It is evident that this dihydrate did not rearrange appreciably before addition of liquid water.

When excess liquid water is added to a suspension of K_2O_2 in liquid ammonia, oxygen appears in proportion to the excess of water over that required for the dihydrate, the oxygen being evolved after evaporation of the ammonia and warming to room temperature. In this case, however, the dihydrate rearranges to K_2O_4 according to equation (7), below.

This is indicated by the fact that the oxygen evolved in stage 1 is invariably approximately twice that evolved in stage 2. The following data serve as example: K_2, 4.45; H_2O in NH_3, 9.36; O evolved *in vacuo*, 0.45; O stage 1, 2.61; O stage 2, 1.35; total O, 4.41.

As may be seen, the total amount of oxygen evolved corresponds closely to that required for K_2O_2 and the amount evolved in stage 1 is very nearly twice that evolved in stage 2. The amount of oxygen evolved *in vacuo*, 0.45 atom, corresponds approximately to the excess of water over that of the dihydrate, 0.36. In other cases, where the excess of water was larger, corresponding results were obtained.

Potassium Trioxide Monohydrate, $K_2O_3 \cdot H_2O$.—Potassium dioxide was oxidized to K_2O_3 and the oxide was treated with water in liquid ammonia. No oxygen was evolved on evaporating the ammonia and warming to 25°. The product was decomposed and the oxygen evolved determined. The data follow: K_2, 4.77, 4.75; total O at K_2O_3 stage, 13.88, 14.36; O/K_2, 2.91, 3.02; H_2O in NH_3, 4.10, 4.23; O stage 1, 3.91, 4.12; O stage 2, 4.53, 4.48; total O, 8.44, 8.60.

Somewhat more oxygen was evolved in stage 2 than in stage 1, which indicates incomplete oxidation of K_2O_2 to K_2O_3. The data indicate that $K_2O_3 \cdot H_2O$ is formed and that this compound does not rearrange under the conditions of the experiment. When excess water is added in liquid ammonia, oxygen is evolved at 25° in proportion to the excess of water added. The remaining product rearranges to K_2O_4 (equation (8), below) as is indicated by the fact that the ratio of oxygen in stages 1 and 2 is 2:1. The data follow: K_2O_3, 3.11; H_2O in NH_3, 6.24; O evolved at 25°, 2.91; O stage 1, 2.19; O stage 2, 1.13; total O, 6.23; $2 \times K_2$, 6.22.

The total O evolved corresponds closely to that required for K_2O_3; the residual product, however, had evidently rearranged to K_2O_4.

VI. Rearrangement of the Hydrated Oxides

The hydrates of K_2O_2 and K_2O_3 rearrange slowly at ordinary temperatures in the dry state with the formation of K_2O_4 and KOH, which is partly or wholly hydrated depending upon the amount of water available.

Rearrangement of $K_2O_2 \cdot H_2O$.—A sample of the hydrated oxide, on standing *in vacuo* for ten days, evolved no oxygen, and on admitting oxygen it absorbed 0.3 mg. The nature of the final product was determined by decomposing with water; the data follow: K_2O_2, 6.30; H_2O 6.20; O stage 1, 4.20; O stage 2, 2.07; total O, 6.27.

The oxygen ratio of 2:1 in stages 1 and 2 shows that practically all of the free oxygen was present as K_2O_4 and rearrangement, accordingly, must have occurred according to the equation

$$3(K_2O_2 \cdot H_2O) = K_2O_4 + 4KOH + H_2O \qquad (6)$$

Rearrangement of $K_2O_2 \cdot 2H_2O$.—The dihydrate rearranges more slowly than the monohydrate. A sample, on standing *in vacuo* for eight days, evolved no oxygen. On decomposing, the following results were obtained: K_2O_2, 3.97; H_2O, 7.59; O stage 1, 2.69; O stage 2, 1.26; total O, 3.95. The total oxygen evolved corresponds closely to that required for K_2O_2 and the amount of oxygen evolved in stage 1 is slightly greater than twice that of stage 2; this is probably due to a slight decomposition of K_2O_2 on addition of water. Rearrangement evidently occurred according to the equation

$$3(K_2O_2 \cdot 2H_2O) = K_2O_4 + 2(K_2O \cdot 3H_2O) \qquad (7)$$

Rearrangement of $K_2O_3 \cdot H_2O$.—This hydrate rearranges more slowly than either of the hydrates of K_2O_2. A sample was allowed to stand *in vacuo* at 25° for seven days, when it was treated with water with the following results: K_2O, 4.18, O abs. by K_2O_2 (vol.), 4.07; H_2O, 3.80; O stage 1, 5.04; O stage 2, 3.10; total O, 8.14.

Some rearrangement evidently occurred since only 4.07 m. atoms of oxygen were added to K_2O_2 while 6.04 m. atoms were evolved on adding water. Rearrangement was incomplete as indicated by the oxygen ratio of stages

1 and 2. Partial rearrangement evidently occurred according to the equation

$$3(K_2O_3 \cdot H_2O) = K_2O \cdot 3H_2O + 2K_2O_4 \qquad (8)$$

Summary

Improvements in the method of preparing K_2O_2 and K_2O_4 by oxidation of the metal in liquid ammonia are briefly described.

The existence of the following compounds has been established: K_2O_3, $K_2O_2 \cdot H_2O$, $K_2O_2 \cdot 2H_2O$ and $K_2O_3 \cdot H_2O$.

The properties and reactions of these compounds are described.

PROVIDENCE, R. I. RECEIVED SEPTEMBER 6, 1934

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Kinetics of the Thermal Hydrogen–Chlorine Reaction

BY ROBERT N. PEASE

Previous studies of the combination of hydrogen and chlorine in heated glass vessels are in disagreement as to the kinetics of the process. Sirk[1] found the initial rate to be proportional to the chlorine concentration and independent of the hydrogen. Hydrogen chloride and oxygen were without effect on the rate. He, therefore, wrote

$$d[HCl]/dt = k\,[Cl_2]$$

Melander[2] reports the reaction to be bimolecular

$$d\,[HCl]/dt = k[H_2][Cl_2]$$

Sachtleben[3] first recognized the strong inhibition by oxygen. He found for the rate in presence of oxygen

$$\frac{d\,[HCl]}{dt} = k\,\frac{[H_2][Cl_2]}{[O_2]}$$

Christiansen[4] in a rather more comprehensive investigation came to the conclusion that the rate in presence or absence of oxygen could be represented by the equation

$$\frac{d\,[HCl]}{dt} = k\,\frac{[Cl_2]}{[HCl] + k'[O_2]}$$

In view of these contradictory conclusions, further investigation of the reaction seemed to be in order. Accordingly a series of flow experiments has been carried out at atmospheric pressure. Previous studies were all by the static method.

Apparatus and Method.—The apparatus was of a conventional type for flow experiments. The reaction tube was of Pyrex glass (15 cm. long, 3 cm. diameter, cleaned with hot nitric acid). It was held at constant temperature (±0.3°) in an electrically heated tube furnace. The gases were separately preheated within the furnace in bulbs joined to one another and to the reaction tube by capillary tubing.

Hydrogen and oxygen were prepared by electrolysis of 30% potassium hydroxide solution between nickel wire electrodes. They passed through hot platinized asbestos and calcium chloride for purification. Rates of flow were determined by current input.

Chlorine was obtained from a tank, and was passed in through a resistance-tube flowmeter. It was dried over calcium chloride. Two tanks of chlorine, the one nearly empty and the other full at the start of the experiments, were used without noticeable difference. This is taken to indicate that both supplied chlorine of high purity. Both tanks were "blown off" before use.

Nitrogen was also obtained from a tank and passed in through a flowmeter. It entered the apparatus with the hydrogen, passing over platinized asbestos with the latter to remove oxygen.

Chlorine and hydrogen chloride were absorbed from the effluent gas by passing over the surface of a potassium iodide solution (20 g. of KI in 60 cc. of solution). Usually a ten-minute sample was taken. The solution was then made up to 250 cc. of which 50 cc. was taken for analysis. The liberated iodine was titrated with 0.1 *N* thiosulfate after which the acid was determined with 0.1 *N* alkali.

All runs were "bracketed" with standard runs to take account of any drift which might occur.

Results.—The thermal hydrogen–chlorine reaction, like the photochemical reaction, is strongly inhibited by oxygen with consequent alteration in the kinetics. Results without added oxygen are presented in Table I. The data have been calculated in terms of partial pressures in the entering and exit gases. These are entered in this

---

(1) Sirk, *Z. physik. Chem.*, **61**, 545 (1908).

(2) Melander, *Arkiv for Kemi, Mineralogi och Geologi*, **5**, No. 12 (1913–1915).

(3) Sachtleben, Diss., Hannover, 1914. See Christiansen, *Z. physik. Chem.*, **2B**, 405 (1929).

(4) Christiansen, *ibid.*, **2B**, 405 (1929).