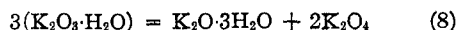


1 and 2. Partial rearrangement evidently occurred according to the equation



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 , $\text{K}_2\text{O}_2 \cdot \text{H}_2\text{O}$, $\text{K}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

The properties and reactions of these compounds are described.

PROVIDENCE, R. I.

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[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. Sirk¹ 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

$$d[\text{HCl}]/dt = k [\text{Cl}_2]$$

Melander² reports the reaction to be bimolecular

$$d[\text{HCl}]/dt = k[\text{H}_2][\text{Cl}_2]$$

Sachtleben³ first recognized the strong inhibition by oxygen. He found for the rate in presence of oxygen

$$\frac{d[\text{HCl}]}{dt} = k \frac{[\text{H}_2][\text{Cl}_2]}{[\text{O}_2]}$$

Christiansen⁴ 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

$$\frac{d[\text{HCl}]}{dt} = k \frac{[\text{Cl}_2]}{[\text{HCl}] + k'[\text{O}_2]}$$

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 ($\pm 0.3^\circ$) in an electrically heated tube furnace. The gases were separately preheated within the furnace in bulbs

(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).

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

TABLE I
 RUNS WITHOUT ADDED OXYGEN

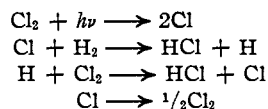
Temp., °C.	Time, sec.	Partial pressures, atm.					$\Delta\text{HCl}/\Delta t$ $\times 10^4$
		Entering		Exit		HCl	
		H ₂	Cl ₂	H ₂	Cl ₂		
Empty bulb							
Composition Varied							
250.0	51.2	0.500	0.506	0.411	0.415	0.180	3.52
	52.6	.754	.253	.677	.175	.155	2.95
	51.1	.250	.756	.189	.696	.121	2.37
	51.1	.500	.506	.404	.410	.193	3.78
Nitrogen Added							
250.0	50.6	0.499	0.501	0.414	0.416	0.170	3.36
	50.1	.247	.506	.195	.453	.105	2.10
	50.8	.500	.251	.449	.200	.101	1.99
	50.7	.499	.501	.407	.409	.184	3.63
Temperature Varied							
250.0	50.7	0.493	0.505	0.391	0.404	0.203	4.01
240.0	51.5	.498	.500	.429	.431	.138	2.68
230.0	52.8	.498	.499	.449	.451	.097	1.84
240.0	51.8	.498	.499	.432	.433	.131	2.53
250.0	50.9	.498	.498	.403	.403	.191	3.75
Time Varied							
250.0	50.4	0.499	0.503	0.415	0.419	0.169	3.35
	101.3	.501	.501	.390	.390	.220	2.17
	156.0	.505	.497	.381	.373	.248	1.59
	50.7	.500	.502	.414	.416	.172	3.89
Packed bulb							
Composition Varied							
250.0	26.5	0.496	0.498	0.451	0.453	0.091	3.44
	26.7	.749	.246	.706	.202	.086	3.22
	26.8	.248	.745	.225	.722	.046	1.72
	26.7	.496	.497	.452	.453	.088	3.30

and succeeding tables along with temperature and time of heating. The latter was calculated in the conventional way. If V is the volume of the bulb and v is the total volume of gas (measured at the temperature and pressure of the experiment) passed per second, then V/v is the heating time in seconds. As will be mentioned later, it is questionable whether such a calculation is perfectly valid. Values of $\Delta\text{HCl}/\Delta t$, the average rate for the experiment, appear in the last column of the table.

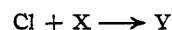
The data of the first two "brackets" of Table I show that the reaction is approximately second order. In the first bracket 75-25% mixtures were compared with 50% mixtures. The rates should stand in the ratio of 0.75 to 1.0. It will be seen that with excess hydrogen the rate is 0.84 of the standard (50% mixture), while with excess chlorine the ratio is 0.63 of the standard. In the second bracket, half of one gas was replaced by nitrogen and the rate compared with a 50% mixture. The rates in presence of the nitrogen

should be 0.5 of the rate with the 50% mixture. The observed values are 0.63 (excess chlorine) and 0.55 (excess hydrogen).

This result recalls the work of Bodenstein and Unger⁵ on the photochemical reaction in absence of oxygen, which reaction was also found to be second order. These authors suggest the mechanism



or

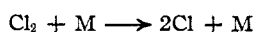


The substance X was suspected of being a compound of silicon.

The corresponding mechanism for the thermal reaction calls for the thermal dissociation of chlorine as primary reaction. Christiansen has considered this question and concludes that the homogeneous dissociation does not occur suffi-

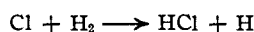
(5) Bodenstein and Unger, *Z. physik. Chem.*, **11B**, 253 (1930-1931).

ciently rapidly. The author agrees with this conclusion. The reaction



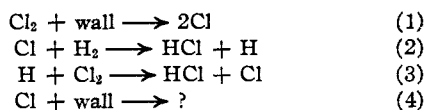
where M is some other molecule, requires an activation energy equal to the dissociation energy of chlorine (57,000 cal. per mole). The maximum calculated rate of dissociation is only 10^{-14} of the observed rate of formation of hydrogen chloride. Thus, either chains are 10^{14} molecules long (they are only 10^5 in the photochemical reaction with pure gases) or the homogeneous dissociation is not the starting mechanism. In addition, the activation energy for the over-all reaction would approximate to 57,000 cal., whereas the value calculated from the observed temperature coefficient (third "bracket," Table I) is only 20,000 cal. On the other hand, there is no obvious objection to assuming that the primary dissociation of chlorine occurs at the walls of the reaction vessel.

We may now note that packing the reaction bulb with broken Pyrex glass does not alter appreciably the rate in absence of oxygen (first and last "brackets," Table I). Granting that chains start at the walls, the result means that chains end on the walls also. However, we cannot assume that the latter process is the recombination of chlorine atoms. This would be equivalent to assuming an equilibrium concentration of chlorine atoms in the gas phase. The reaction



would then become the rate-determining process. The over-all rate would involve the term $[\text{Cl}_2]^{1/2}$, and the main contribution to the activation energy would be one-half the dissociation energy of Cl_2 (28,500 cal.). Actually the rate is approximately proportional to the first power of the chlorine concentration, and the observed activation energy is less than the required value. We must, therefore, assume a reaction for stopping chains which involves the actual removal of a chain carrier—either H or Cl. The simplest assumption to make is that chlorine atoms form a compound such as silicon chloride at the surface.

We will write for the mechanism



These equations lead without approximation to the expression

$$\frac{d[\text{HCl}]}{dt} = \frac{2k_1k_2}{k_4} [\text{H}_2][\text{Cl}_2]$$

Christiansen applies the equation

$$\frac{d[\text{HCl}]}{dt} = k \frac{[\text{Cl}_2]}{[\text{HCl}]}$$

to his data for the rate in absence of oxygen. The resulting values of the constant are not in good agreement. Better agreement is obtained with the author's equation, which fact may be taken as further evidence of its substantial correctness. Table II is borrowed from Christiansen's Table 4, No. 2, p. 416. Average pressures are shown, as well as average rates. The units are cm. and time in minutes. The temperature was 200.8° . Values of Christiansen's constant appear in the next to last column, and of the author's constant in the last column.

TABLE II
CHRISTIANSEN'S DATA IN ABSENCE OF OXYGEN

Average pressure, cm.			Rate $\times 10^2$	k $\times 10^2$	$\frac{2k_1k_2}{k_4}$ $\times 10^2$
H_2	Cl_2	$\frac{1}{2}\text{HCl}$			
17.82	25.30	0.33	13.3	0.17	0.30
14.22	20.44	1.49	7.29	.53	.25
10.71	16.05	2.78	4.65	.80	.27
8.26	12.90	3.46	3.00	.80	.28
6.45	10.48	3.72	2.17	.77	.32
5.08	8.57	3.74	1.60	.70	.37

When runs were made at successively longer times (fourth bracket, Table I), the yield fell off far more rapidly than one would expect for a second-order reaction. This seemed to suggest that the product of reaction was inhibiting. To test this point, hydrogen chloride was added to the entering gases, and the rate of reaction compared with that when an equal amount of nitrogen was added. Hydrogen chloride was introduced by bubbling the entering hydrogen through concentrated hydrochloric acid held at the requisite temperature and then passing over calcium chloride to remove water vapor. The results were not too satisfactory because of the difficulty of controlling the addition of the hydrogen chloride. However, it is probable that *more* chlorine reacted in presence of $\frac{1}{3}$ atm. of hydrogen chloride than in presence of the same amount of nitrogen. It may be taken as certain that hydrogen chloride has no marked inhibiting action. The apparent slowing down of the reaction at lower flow rates is presumably bound up with the characteristics of the flow through the reaction tube. Similar results have been observed before.⁶

(6) E. g., Pease and Durgan, THIS JOURNAL, 52, 1262 (1930), on the dissociation of paraffin hydrocarbons.

Effect of Oxygen.—Addition of as little as 1% of oxygen to hydrogen and chlorine reacting at 250° was found to reduce the yield of hydrogen chloride to practically zero. The temperature had to be raised over 100° to restore the rate. At 360° a series of runs were made on mixtures containing 1 part oxygen to 10 parts of reaction mixture. Results appear in Table III.

TABLE III
REACTION IN PRESENCE OF OXYGEN
1 part oxygen to 10 parts reaction mixture

Temp., °C.	Time, sec.	Partial pressures, atm.					HCl/l × 10
		Entering H ₂	Entering Cl ₂	H ₂	Exit Cl ₂	HCl	
Empty bulb							
Composition Varied							
360.0	37.9	0.448	0.458	0.421	0.432	0.052	0.14
	37.8	.675	.229	.652	.206	.047	.12
	37.8	.222	.684	.199	.660	.047	.12
	37.8	.448	.457	.428	.437	.039	.10
Packed bulb							
Composition Varied							
360.0	19.8	0.454	0.456	0.273	0.275	0.362	1.83
	19.9	.685	.226	.592	.133	.185	0.93
	20.0	.227	.684	.056	.513	.341	1.71
	19.9	.455	.456	.314	.315	.283	1.42

In this case, it was almost impossible to obtain good "brackets." Even after running for six to eight hours, a slow drift to lower conversions continued. In spite of this, the results show definitely an *acceleration* of reaction by packing. The packing material was Pyrex broken to pieces of 4-10 mesh. It was estimated that the surface was thereby increased some 5 to 10 times. The observed acceleration averages to something over 10.

We assume that, in presence (as in absence) of oxygen, chains start on the walls. They are ended by oxygen in the gas phase, as has been assumed for the photochemical reaction.⁷ If this is the case, packing should accelerate in presence of oxygen by increasing the rate of the primary reaction. Chains, being ended in the gas phase by oxygen, never get to the walls. Hence chain-breaking at the walls is not a factor.

It was of interest to determine how much oxygen was consumed in the process of breaking chains. To this end, a series of experiments was carried out at 370° with a mixture of 2H₂:1Cl₂:1O₂.

(7) Bodenstein and Schenk, *Z. physik. Chem.*, **20B**, 420 (1933).

After absorption of chlorine and hydrogen chloride in potassium iodide solution, the residual gases were collected, measured and analyzed. The precision of the experiment was not sufficiently high to detect any loss of oxygen. In one case, when 5.0 cc. of hydrogen had been used in reaction, less than 0.2 cc. of oxygen disappeared. Thus, the ratio of hydrogen (or chlorine) used to oxygen used is at least of the order of 25 or 50 to 1. An examination of the data of Bodenstein and Schenk on the consumption of oxygen in the photochemical reaction reveals ratios of this order of magnitude.

In view of the poor agreement in the "check" runs, not much can be said as to the kinetics in presence of oxygen. A change in composition from 75-25% mixtures to 50% mixtures did not greatly alter the yield of hydrogen chloride in the empty bulb. Such change as occurred is in the direction of proportionality to chlorine concentration. Christiansen writes

$$\frac{d[\text{HCl}]}{dt} = k \frac{[\text{Cl}_2]}{[\text{O}_2] + k'[\text{HCl}]}$$

The runs give no evidence against the validity of this equation, though in view of the results in absence of oxygen, it is doubted that hydrogen chloride has any appreciable inhibiting action.

Summary

1. The thermal hydrogen-chlorine reaction in Pyrex vessels has been studied by the flow method in presence and absence of oxygen, and with and without a broken Pyrex packing.
2. Oxygen strongly inhibits reaction.
3. A packing does not affect the rate in absence of oxygen but accelerates reaction in presence of oxygen.
4. In absence of oxygen, the reaction is approximately second order. Hydrogen chloride is not an inhibitor.
5. In presence of oxygen, results were clouded by a slow drift in activity. The reaction kinetics are in the direction of proportionality to the chlorine concentration.
6. No appreciable amount of oxygen is consumed (as compared to hydrogen or chlorine) in the process of inhibition.