Rates of Hydrogen Chloride Oxidation

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Rates of oxidation of hydrogen chloride (the Deacon process) were measured in a recycling reactor with chromic oxide catalysts. The temperatures were 325° to 355°C., and a wide range of reactant compositions was used. The reverse reaction was also explored at 355° to 370°C. The experimentation was carefully tested to be sure that the construction material did not affect the results and that diffusional effects were absent.

An empirical equation is described which correlates well the rates of oxidation and fits the original observed data. It is capable of predicting reasonably well some of the observed rates of the reverse reaction.

The reaction $2HCl + \frac{1}{2}O_2 = Cl_2 + H_2O$ has been known for over a century. Interest in it has been revived recently because of the abundance of the by-product hydrogen chloride from chlorination processes, since hydrogen chloride can be converted to chlorine for reuse with obvious advantages. While the thermodynamics of this reaction is well known (*1*), information about the rate of the reaction is extremely scarce, and the measurement and correlation of reaction rates were the primary purpose of this study.

SCOPE

Conversion vs. time data were observed for this reaction at the following conditions:

Temperature: 325°, 340°, and 355°C. Reactant ratio with air: stoichiometric, 3/1, and 1/3. Oxygen-enriched air: stoichiometric ratio with 30 and 40% oxygen-enriched air. Catalyst: 15.55 g. of a commercial chromic oxide supported on alumina (Girdler G-41), 10% chromic oxide; also Girdler T-564, 15% chromic oxide. The B.E.T. surface area of the former was 138 sq. meters/g. and the diffusivity for hydrogen at room temperature in a Wicke-Kallenbach apparatus was 0.68 sq.cm./sec. Runs were also made with chlorine and water added to the feed. Runs were made for the *reverse* reaction at the following conditions: temperature: 355° and 370°C.; chlorine to water ratio: 1/1 and 3/1; catalyst: 15.55 g. of Girdler G-41 as above.

EXPERIMENTAL

Apparatus

The apparatus, very similar to that used by Butt, Bliss, and Walker (*3*), is illustrated in Figure 1. The reactor proper was constructed of 35-mm. diameter Pyrex tubing, although the inlet line and sampling port (sealed with a serum stopper) were 10 and 7 mm., respectively. The U-tube section was connected to the rest with standard ground glass joints. The catalyst bed (15.55 g. and ¾-in. depth in all but one run) was supported on a glazed porcelain perforated disk, which was, in turn, supported on indentations in the glass tubing. Gas flow was downward through the catalyst. The nickel-sheathed, chromel-alumel thermocouple of 1/16-in. O.D. was sealed into position so that the temperature of the center of the catalyst bed was measured. The total volume of the system was about 2,400 ml.

The gas was circulated with a Vanton Flexiliner pump, Model XB-T120, with a Teflon body block and a Viton-A liner. Connections to the glass were accomplished with Teflon tubing, sealed with epoxy resin.

The Ashcroft chemical pressure gauge had a corrugated diaphragm made of tantalum-clad beryllium in place of a Bourdon tube. Other parts of the gauge were made of Hastelloy B. It was graduated to 0.2 lb./sq. in.

A molten tempering salt bath was contained in a 12-in. diameter by 14-in. deep insulated tank which could be raised to surround the U-tube section. It was heated with two 1,000-w. Calrod heaters, one of which was controlled through a bimetallic regulator. The bath was agitated. Additional heating of the glass assembly to prevent water condensation was found necessary, and was accomplished with Brisheat flexible heating tapes, controlled with powerstats.

The feed system was constructed largely of 10 mm. Pyrex tubing and suitable stopcocks. The charge tank was a stainless steel sampling cylinder of 3,750 ml. volume.

Materials

Hydrochloric acid, chlorine, and air were supplied in cylinders from the Matheson Company, and nitrogen and oxygen from Air Reduction Company. The catalyst was supplied by the Girdler Corporation, G-41 containing 10% chromic oxide on alumina, and T-564 containing 15% chromic oxide on alumina. Both were supplied as ¼-in.-diameter by ¼-in.-long cylinders. No special activation procedure was required.

Analysis

Analyses were made with a Model 21, all-glass chromatograph made by F. & M. Scientific Corporation. The adsorbent was silicone grease on Haloport F; the column length was 8 ft. The chromatograph was coupled with a Leeds and Northrup Speedomax type G Recorder with a mechanical disk integrator. Calibration was accomplished by comparing peak areas with known sample amounts of the pure gases. Only hydrogen chloride, chlorine, and air were analyzed; no attempt to analyze for water was made with this column. This reaction is free from side reactions, so it was possible and advantageous to weigh the hydrogen chloride and chlorine analyses more heavily than that of air. The hydrogen chloride and chlorine compositions, determined accurately from the peak areas, were used to calculate the fractional conversion and this, along with the composition of the initial charge, permitted the calculation of the number of moles of oxygen, nitrogen, and water in the samples.

Procedure

Gas mixtures of hydrogen chloride and air (and chlorine if desired) were prepared in a feed cylinder by introducing

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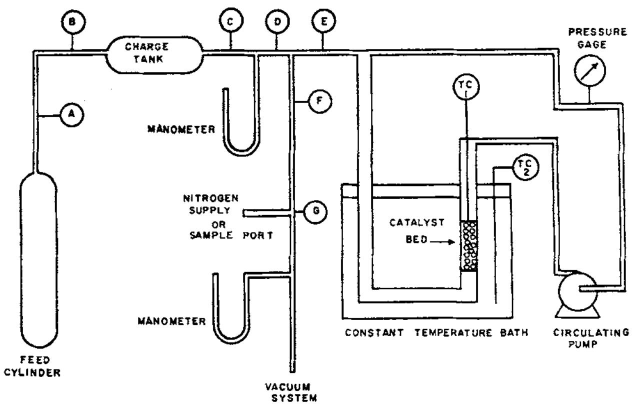

Fig. 1. Diagram of reactor and charge system.

the individual gases separately. The pressure was high enough to permit the withdrawal of several reactant charges. The contents were analyzed several times to insure consistent results, indicating complete mixing. Such mixing required about 16 hr. A few runs were made with water added to the system. In these cases the feed gas mixture (hydrogen chloride and oxygen for the forward reaction; chlorine for the reverse reaction) was introduced as above and liquid water was injected directly into the reactor system through the sample port with a hypodermic syringe.

The run proper was begun by bringing the reactor and bath to the desired temperature. Then the charge tank and lines were evacuated by opening valves *C, D, F,* and *G* (Figure 1). Valve *D* was then closed and the charge tank and lines up to *D* were filled with the proper charge from the feed cylinder to a pressure of about 800 mm. Hg gauge. Valves *A* and *B* were then closed and valve *E* opened to permit evacuation of the reactor proper which contained the gas of a previously completed run or nitrogen during idle periods. The pressure in the reactor was reduced to less than 1 mm. Hg. Valves *F* and *G* were then closed and *D* opened to permit the admission of the feed gas. Valve *D* was then closed and the pump started; measurements of catalyst temperature and of pressure were made after 1 min. and after every 3 min. thereafter. Samples were withdrawn through the serum stopper in the sample port with a 1-ml. hypodermic syringe immediately following each temperature and pressure measurement. When the run was completed the gas contents were evacuated and nitrogen for storage was introduced unless an immediately following run was planned.

Before and after the filling operation, the pressure and temperature of the contents of the charge tank were measured. These with the ideal gas law assumption permitted calculation of the amount of charge.

The number of 1 cc. samples withdrawn never exceeded 20; thus, the amount withdrawn never exceeded 1% of the total charge.

PRELIMINARY OBSERVATIONS

Catalyst Behavior

The copper catalysts which are widely used for this reaction volatilize in part during use. Such behavior could not be tolerated in studies of this sort. Accordingly, preliminary runs were made with the chromic oxide catalysts used here and then repeated with the catalyst removed. Any volatilization would have resulted in condensation in the colder parts of the system (which might not necessarily be visible) and in consequent catalytic activity after removal of the catalyst. No conversion was found when the catalyst was removed, and it must be concluded that the catalyst was not volatile.

The stability of the catalyst was excellent. Runs were reproducible within experimental error as long as they were not separated by more than 16 hr. If a longer time elapsed, storage under nitrogen followed by one wasted or dummy run immediately restored the catalyst to its former activity. Reproducibility within experimental accuracy was tested and proved with runs as much as a month apart, as long as this storage and restoration procedure was followed.

Construction Materials

While an all-glass system would be preferable, it is not possible in a system of this complexity. The Viton-A liner, serum stopper, the tantalum cladding, and the epoxy resin used for certain seals could be suspected of introducing possible catalyst poisons or of removing by adsorption some of the components of the reaction. There was never any evidence of either of these phenomena. Absence of catalyst poisoning was demonstrated by the remarkable stability of the catalyst. Absence of significant adsorption on these substances was demonstrated by: (1) Recycling hydrogen chloride and air mixtures at reaction temperature with no catalyst. The pressure remained constant, indicating negligible adsorption. (2) Recycling nitrogen and water vapor mixtures at reaction temperature for 20 min. to promote water adsorption, if it were to occur. Water partial pressure was as high as 0.43 atm., much higher than that found as a consequence of the forward reaction. The system was then evacuated, the vacuum pump stopped, and pressure buildup checked. The rate of pressure buildup (due to slight leaks which were unavoidable with such a pressure difference) was the same as that with the recirculation of pure nitrogen in blank runs. Thus water adsorption was absent. This was confirmed by other items of indirect evidence. It is an important point because water compositions were calculated from the stoichiometry of the reaction and were not analyzed.

Absence of Diffusional Effects

In work of this sort it is essential to have some assurance that rates of reaction and not rates of diffusion are the dependent variables measured. Fluid diffusional effects were explored experimentally and theoretically. The pump was operated at several speeds and the velocity of the gases measured and shown to be approximately linear in the pump speed. The course of the reaction was followed at pump speeds of 233 and 355 rev./min. and no difference in conversion vs. time curves (within experimental error) was observed. Ensuing runs were made at 355 rev./min. Calculations according to the methods of Yang and Hougen (*10*) showed the ratio of the pressure drop of reactants between main body of the gas and catalyst particle to the total pressure was less than 0.01 at the *highest initial rates.*

Pore diffusion was also explored experimentally and theoretically. The catalyst particles were cut in half so that the length was cut from ¼ in. to ⅛ in. No change in rate was observed. Also, calculations according to criterion of Weisz (*9*) indicated an effectiveness factor of 0.9 or higher. In these calculations a measured diffusivity (*4*) of 0.68 sq.cm./sec. was used. This diffusivity was determined in a Wicke-Kallenbach experiment with hydrogen and helium at room temperature. Knudsen diffusion was assumed in calculating the diffusivity under reaction conditions.

It thus seems reasonably sure that detailed interpretation of the rate data can be made with confidence that the catalyst was nonvolatile and stable and not poisoned by nonglass construction materials, and that the rates measured were reaction rates, not those of fluid or pore diffusion.

DATA

Fifty-eight runs were made. The forward reaction was studied at 325°, 340°, and 355°C. and at initial pressure

TABLE 1. SAMPLE OF ORIGINAL DATA

Run 4J
Temperature of catalyst bed: 355°C.
Initial pressure: 1,010 mm. Hg
Catalyst: 15.55 g. G-41
Composition of feed:

	mole %	g.-moles
Hydrogen chloride	20.3	0.0199
Air	79.7	0.0783

	g.-moles in reactor			
Time, min.	Hydrogen chloride	Oxygen*	Chlorine†	Total pressure, mm. Hg
1	0.01668	0.01559	0.00161	995
4	0.01054	0.01406	0.00468	950
7	0.00783	0.01338	0.00604	931
10	0.00637	0.01301	0.00677	920
13	0.00540	0.01277	0.00726	914
16	0.00475	0.01262	0.00756	910
20	0.00415	0.01247	0.00786	906
25	0.00344	0.01229	0.00822	902
30	0.00290	0.01215	0.00850	899
35	0.00267	0.01209	0.00862	897
40	0.00209	0.01194	0.00892	896

* Calculated by difference.

† Moles of water taken as equal to moles of chlorine.

of 989 to 1,075 mm. Hg. All runs but two were with 15.55 g. Girdler G-41, 10% chromic oxide catalyst. Those two were with 16 g. Girdler T-564, 15% chromic oxide. The catalyst size in all runs was either ¼ in. diameter by ¼ in. long or ¼ in. diameter by ⅛ in. long, and it has been noted above that these sizes exhibited the same rates. Feed compositions were varied over wide ranges. Stoichiometric mixtures of air and hydrogen chloride (46% hydrogen chloride), excess air mixture (20 mole % hydrogen chloride), excess hydrogen chloride mixtures (49, 54, and 72 mole % hydrogen chloride), and enriched air-hydrogen chloride mixtures (oxygen–nitrogen = 30/70 and oxygen–nitrogen = 40/60, 60.9 mole % hydrogen chloride) were used. In addition, product chlorine or product water was added to the reactants in certain runs. It is apparent that the composition variable was tested very severely. The reverse reaction, that is $Cl_2 + H_2O = 2HCl + \frac{1}{2} O_2$, was studied at 355° and 370°C. and at initial pressure of from 884 to 911 mm. Hg. Only four runs were made here with chlorine-water ratios of 1.0 and 3.0. The details of all run conditions and the conversion-time data are given by Jones (6). Data of a sample run are given in Table 1.

INTERPRETATION OF DATA

Observations

Some semiquantitative observations were made first as to the importance of certain variables. Curves of moles of hydrogen chloride vs. time showed clearly that: (1) Higher temperatures greatly accelerated the rates. (2) Excess oxygen accelerated the rate. (3) Excess hydrogen chloride retarded the rates. (4) Water in the feed retarded the rates. (5) Runs made with chloride added to the feed, preserving the same partial pressures of oxygen and hydrogen chloride as used without chlorine, exhibited no observable difference in rates from those runs without chlorine. (6) Same as (5) with nitrogen instead of chlorine.

A quantitative interpretation was begun with rates, not conversions. These rates were determined from the basic conversion vs. time curves as follows: (1) A plot was made of number of moles of *oxygen* in the recycling stream vs. time. In many cases the results of several runs made under identical conditions were plotted on the same sheet. (2) A smooth monotonic line was drawn on this plot by eye. (3) The points of this curve at equal time intervals were differentiated numerically (Newton's method for early parts of the curves and Stirling's for the later parts).

The resulting rates, expressed as g.-moles oxygen/(min.) (g.-catalyst), were thus established for a variety of time points at which the partial pressures of the various components had been measured and recorded in the original data. A few sample rates are given in Table 2. These runs are also portrayed in later figures. The determination of rates from conversion data is subject to considerable error. Accordingly, these rates were checked by integration to establish how well the original data could be reproduced. With the various samples tried the original data were reproduced within a few percent.

The alternate method, which involved fitting a curve to the data points by the least squares method (machine

TABLE 2. REPRESENTATIVE CONDITIONS AND RATE DATA
In all cases, 15.55 g.-catalyst, 10% chromic oxide

Run No.	3M	3T	3II	4J	4FF	4N
Temperature, °C.	355	340	325	355	325	355
Initial pressure, mm. Hg	991	1,014	1,012	1,010	1,004	1,010
Feed components:						
Mole % hydrochloric acid	45.4	45.4	44.3	20.3	21.5	73.3
Mole % air	54.6	54.6	55.7	79.7	78.5	26.7

$$\text{Rates, } \frac{\text{g.-moles oxygen}}{(\text{min.})(\text{g.-catalyst})} \times 10^5$$

Time, min.						
0	3.82	3.22	2.71	5.83	6.64	1.35
1	3.69	3.0	1.15	4.4	—	—
2	—	—	—	—	2.69	1.25
4	2.74	1.9	0.61	2.25	—	—
5	—	—	—	—	1.44	—
7	1.88	1.23	0.46	1.15	—	—
10	1.32	—	0.40	0.67	0.66	0.74
13	1.27	0.72	0.15	0.35	—	—
20	—	—	—	—	0.37	—

computation) and analytical differentiation of this was tried. In several instances, reasonable agreement between the two methods was found, but in other cases the analytical differentiation of a least squares polynomial led to absurd results, for example, negative rates at some points. The latter method was thus abandoned in favor of the former.

Initial Rates

Rates at zero conversion are subject to more error than later rates, but they are useful for preliminay obsevations as to the form of a rate equation. The usual Hougen and Watson procedure (5) was followed and the equation

$$r_o = \frac{k\,p_A^{1/2}}{1 + \beta p_B} \tag{1}$$

in which A refers to oxygen and B to hydrogen chloride was shown to fit the data better than other forms tried. This equation was linearized to

$$\frac{p_A^{1/2}}{r_o} = \frac{1}{k} + \frac{\beta p_B}{k} \tag{2}$$

It was in this form that the superior agreement with the data when compared to other possible linearized equations was observed. This superiority was demonstrated at all three temperatures. It should be noted that this equation is consistent with the observations noted above, that oxygen accelerated and hydrogen chloride retarded the rates.

Rates Over Full Conversion Range

The equation form found in the treatment of initial rates suggested the following as an equation possibly applicable to the entire array of rate data:

$$r = \frac{\left[k \quad p_A^{1/2} - \left(\frac{p_C p_D}{p_B^2 K}\right)\right]}{1 + \beta p_B + \gamma p_C + \frac{\alpha p_C p_D}{p_B^2 K}} \tag{3}$$

in which C and D refer to water and chlorine, respectively. The above form meets the following requirements or observations: zero rate at equilibrium; acceleration of rates with excess oxygen; deceleration of rates with excess hydrogen chloride or water; and very small or negligible effect of chlorine or nitrogen on the rate, at least at conversions far from equilibrium. This equation is of the usual form, but in this case the constants α, β, and γ *are empirical constants only* and not adsorption equilibrium constants. This will be discussed more fully below.

TABLE 3. VALUES OF THE CONSTANTS
The three values are for 325°, 340°, and 355°C.

Constant	Value
k, g.-moles oxygen/(min.) (g.-catalyst)(atm.)$^{1/2}$	$0.26 \times 10^{-4} \pm 0.05 \times 10^{-4}$*
	$0.92 \times 10^{-4} \pm 0.18 \times 10^{-4}$
	$2.8 \times 10^{-4} \pm 1.1 \times 10^{-4}$
α, atm.$^{-1/2}$	18 ± 30
	142 ± 42
	230 ± 95
β, atm.$^{-1}$	0.01 ± 1.1
	0.22 ± 1.1
	3.1 ± 2.4
γ, atm.$^{-1}$	11 ± 6.1
	21 ± 6.6
	25 ± 12.8
K†, atm.$^{-1/2}$	35.7
	26.7
	20.3

* The ± values represent twice the standard deviation.
† The equilibrium constant from Arnold and Kobe (1).

This equation can be rearranged to

$$\frac{p_A^{1/2} - \frac{p_C p_D}{p_B^2 K}}{r} = \frac{1}{k} + \frac{\beta}{k} p_B + \frac{\gamma}{k} p_C + \frac{\alpha}{k}\frac{p_C p_D}{p_B^2 K} \tag{4}$$

The value of the equilibrium constant K is known from Arnold and Kobe (*1*); the values of all the partial pressures constitute the original observations, and the rates r are available by the methods described. The above equation is linear in the independent variables $\frac{p_C p_D}{p_B^2}$, p_B, and p_C and the constants may be determined by the least squares method. Such a method assumes no error in these independent variables; this was not strictly the case, but there is much less error in them than in the rates.

The constants thus determined are listed in the next section.

RESULTS AND DISCUSSION

Constants of the Rate Equation

The constants in the above rate equation are given in Table 3.

It should be noted that these constants were determined with the least squares method on the linearized form of the rate equation, Equation (4). They are not the least squares constants for the original rate equation, Equation (3). The magnitudes of the standard deviations, determined with methods described by Mickley, Sherwood, and Reed (7), should also be noted. Their large values reflect random errors which are not inconsiderable. The attempt was made to use the nonlinear least squares method to get appropriate constants for the nonlinear rate equation, Equation (3). It was unsuccessful because convergence was not attained. The neglect of higher terms in the Taylor expansion proved unwarrented, because the first values reported here are simply not close enough to the proper values.

The behavior of α, β, and γ with temperature must be noted. Since adsorption equilibrium constants should decrease with rising temperature, α, β, and γ are clearly not such and must be regarded as empirical constants only.

It is clear that the measurements of this work require a more thorough reexamination and such work is planned. The principal virtue of the rate equation here reported is its ability to correlate the measured conversion data.

Reproducing the Original Data

An appropriate test of any proposed rate equation and its constants is its application to the original number of moles vs. time data. This was done by integrating graphically Equation (3) to yield number of moles of oxygen vs. time for several runs. The results, compared with the original data, are shown in Figures 2, 3, and 4.

In Figure 2, runs at 325°, 340°, and 355°C. are shown, and the agreement is seen to be good. Similar plots (*6*) showed similar good agreement for most other conditions such as feeds containing water vapor, excess air, and excess oxygen. A particularly severe test is shown in Figure 3 in which excess air was used and equilibrium (about 87.5% conversion) was closely approached.

It must be pointed out that there is one case in which the data are not very well reproduced with this rate equation, the presence of a considerable excess of hydrogen chloride. This is illustrated in Figure 4.

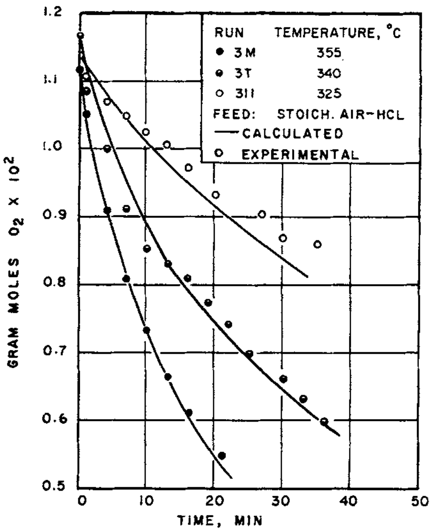

Fig. 2. Comparison of calculated and experimental conversions.

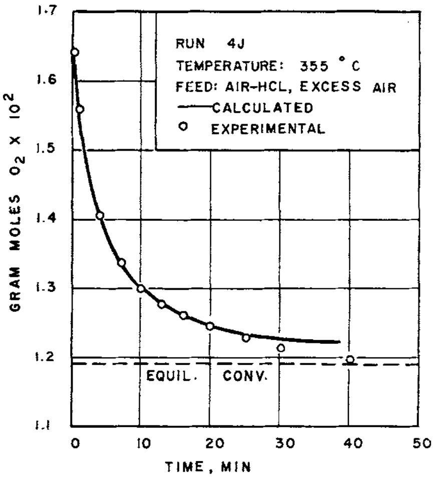

Fig. 3. Comparison of calculated and experimental conversions.

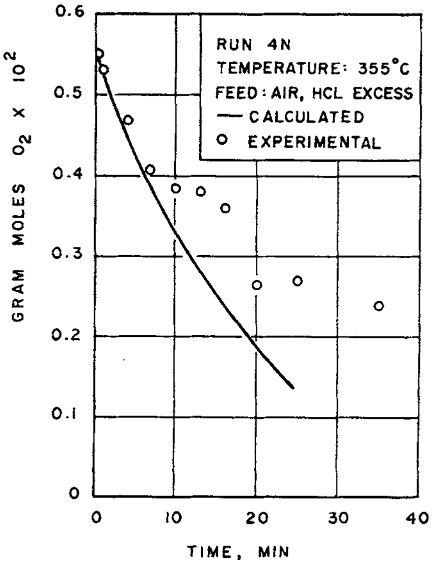

Fig. 4. Comparison of calculated and experimental conversions.

It must be especially noted that in these figures the agreement between observed and calculated partial pressures is shown. It is thus clear that not only the correlating equation is thus tested and shown to be generally good, but also the technique of rate determination.

A more general comparison was afforded by comparing measured values of

$$\frac{p_A^{1/2} - \dfrac{p_C p_D}{p_B^2 K}}{r}$$

with calculated values, with the use of Equation (4).

The average deviations between measured and calculated values for all runs were 14% at 355° and 340°C. and 30% at 325°C.

Activation Energy

A conventional plot of ln k vs. reciprocal temperature permitted the calculation of the activation energy. The result was 58,000 cal./g.-mole. The temperature dependencies of the empirical constants α, β, and γ are not expressible thus; the values of those given in Table 3 are such that interpolation may be permissible, but extrapolation outside the temperature range here used cannot be recommended.

Test of the Rate Equation with the Reverse Reaction

The rate equation here presented is an empirical one, and it would not necessarily be expected to predict the reverse reaction rate very well. It does so, however, to a reasonable degree.

Limitations of the equipment were such that the reverse reaction could not be studied extensively. It was necessary to go to higher temperatures because only there are equilibrium conversions low in chlorine and water. Thus, 355°C., the highest temperature for the forward reaction, became the lowest for the reverse.

The temperature 370°C. was also attempted, but this was very near to the ultimate for this equipment. Furthermore, the rates of reaction were quite slow; the reason for this will be discussed below. Consequently, the accuracy of the reverse reaction measurements was inferior to those of the forward reaction. Our attention was confined to initial rates only, calculated as described previously.

The rate equation, shown to be applicable to the forward reaction, was written backward:

$$r = \frac{k\left[\dfrac{p_C p_D}{p_B^2 K} - p_A^{1/2}\right]}{1 + \beta p_B + \gamma p_C + \alpha \dfrac{p_C p_D}{p_B^2 K}} \qquad (5)$$

When applied to initial rates, that is, $p_A = p_B = 0$, this becomes $r = \dfrac{k}{\alpha}$ (6). It is the presence of the α in the denominator which explains the low rates. When the values determined for the forward reaction are used the initial rate at 355°C. should be

$$1.21 \times 10^{-6} \frac{\text{g.-moles oxygen}}{(\text{min.})\,(\text{g.-catalyst})}$$

$$\text{or } \frac{2.42 \times 10^{-6} \text{ g-moles water}}{(\text{min.})\,(\text{g.-catalyst})}$$

which are now oxygen formed or water consumed. It should be noted that the initial rates should be independent of all partial pressures. The measured initial rate was 2.2×10^{-6} g.-moles water consumed when the feed was stoichiometric and 2.5×10^{-6} when the chlorine-to-water ratio in the feed was 3/1. When the experimental difficulties here are considered, the agreement is good. Comparable measured initial rates at 370°C. were 2.5×10^{-6} and 3.9×10^{-6} g.-moles water consumed/(min.) (g.-catalyst). Comparison with predictions of the forward reaction at 370°C. is not possible, because extrapolation of the various constants beyond the experimental range is not recommended. The agreement between rates measured and those calculated with Equation (5) beyond the initial rates was not good, however.

Comparison with Other Data

As noted before, rate data on this reaction are very scarce, and no data on this reaction in the literature are closely comparable to these. Parthasanathy (8) measured the rates in a fluidized bed of copper oxide promoted with iron oxide and correlated his results with temperature and conversion only (not individual partial pressures) with an empirical equation of unusual form. The rates reported here at roughly comparable conditions (355°C. and zero conversion) are about ten times as great as those reported by Parthasanathy. It is probable that the difference in catalysts and the careful exercise of precautions to minimize diffusional effects used here account for this difference. In a patent issued to Diamond Alkali Company (2), information is given with which a rate can be computed at 428°C. with a 28% chromic oxide catalyst. This rate is about the same as the ones reported here at 350°C. with only 10% chromic oxide. Again, it seems that the rates herein reported are very high relative to the Diamond Alkali work, probably for the same reason.

Experimental Precision

The calibration of the chromatograph indicated an average deviation of about 2% with a maximum, excluding a very few isolated points, of about 4%. The pressure measurements were subject to only 1% deviation. The loss of reacting charge due to sampling and leaks was never over 2%, but, of course, the charge composition is not altered by such withdrawals and the pressure change was measured. Negligible inaccuracies should be assigned to this source. Temperature measurements were precise to within ½%.

The two worst sources of error are both characteristics of the beginning of a run. The first is the zero-time error due to the great number of things which must be done at the start of a run. Zero time may have been in error by as much at 15 sec. which would introduce a considerable error into the initial rates in particular. This is a major reason why initial rates were used only when essential (that is, to get the rough form of the equation.) The major work with the rate equation was done with later rates, where the contribution of this error would vanish.

The other source of significant error at the beginning of a run is that the initial rate of heat generation is the highest of the entire run and must lead to a rise in temperature of the catalyst. This rise has been estimated from measured rates and the heat of reaction to be about 1.5°C. Such a rise should contribute only a 2 to 3% error at 340° and 355°C., but at 325°C., where the rates are lower, this error could amount to 20%.

It is difficult to combine these estimates in the conventional propagation of error calculation, because the rates were calculated by numerical methods applied to a smoothed curve. No simple mathematical function is involved. It seems reasonable, however, to assert that a precision of 10 to 15% should be expected at the two higher temperatures and 30 to 40% at 325°C. This is roughly in conformity with the comparisons between calculated and measured values of

$$\frac{p_A^{1/2} - \dfrac{p_C p_D}{K p_B^2}}{r}$$

It is probable that the precision of the four reverse reaction runs is considerably inferior. The charging operation with appreciable amounts of water was difficult, and the high temperatures gave great difficulties with all measurements.

Effect of Chromic Oxide Content in Catalyst

Only two runs were made with 15% cromic oxide catalyst. The conversion-time curve for this run exhibited slopes rather more than twice those obtained with the 10% chromic oxide catalyst.

CONCLUSION

The use of a recycling differential reactor in a study of the reaction of $2HCl + \frac{1}{2} O_2 = Cl_2 + H_2O$ provided a large body of rate data on the reaction. The data were correlated by an equation derived with the methods of Hougen and Watson, but the equation must be considered to be empirical, since some of the terms which are regarded as adsorption equilibrium constants were found to exhibit improper behavior with temperature. The reverse reaction was also studied.

Further work should be directed to studies of the reverse reaction and correlation of the rates of the forward and reverse reactions. The stability of the catalyst, the absence of side reactions, and the fact that accurate values of the chemical equilibrium constant are available make this reaction scheme particularly attractive for such studies.

ACKNOWLEDGMENT

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NOTATION

α, β, γ = empirical constants in rate equation
r = rate of reaction, g.-moles oxygen/(g.-catalyst) (min.)
k = reaction rate constant for adsorption step rate controlling, g.-moles oxygen/(g.-catalyst) (min.)/atm.$^{1/2}$
p_A, p_B, p_C, p_D = partial pressures of oxygen, hydrogen chloride, water, and chlorine, atm.
K = homogeneous gas phase equilibrium constant, atm.$^{1/2}$

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