

chloride obtained from acetophenone. The dianilide was prepared and its m. p. and mixed m. p. were identical with those of the acetophenonedisulfonyl chloride (209–210°).

Summary

1. The action of chlorosulfonic acid upon acetophenone yields the 2, ω -disulfonyl chloride.
2. Sulfonation of acetophenone with 45%

oleum yields a mixture of the ortho and meta sulfonic acids.

3. By evaporating its aqueous solution to dryness, acetophenone-2, ω -disulfonic acid is converted into the cyclic ketosulfone, 3(2)-thianaphthenone-1-dioxide.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Thermal Hydrogen-Chlorine Reaction.¹ I. Experimental Kinetics

By J. C. MORRIS² AND R. N. PEASE

The thermal reaction between hydrogen and chlorine has received a surprisingly small amount of attention, considering the fundamental theoretical importance of this combination. Older results of Sirk,³ Melander,⁴ and Sachtleben⁵ are of little value, except in a qualitative way. The more recent results of Christiansen⁶ and of Kornfeld and Khodschaian⁷ have been obtained almost entirely for mixtures containing oxygen. Initial concentrations in these two cases were not varied sufficiently to specify a kinetic equation for the pure gases, and an extrapolation to zero oxygen of the equations found for oxygen-containing mixtures yields quite different expressions. Only in the work of Pease⁸ were the starting compositions widely varied, but in this instance the results were only approximate. A thorough investigation of the kinetics of this reaction in order to clear up the discrepancies and to establish the mechanism of the process in the pure gaseous mixture seemed indicated, and was the object of the present research.

Experimental Details.—Experiments were carried out in a static system, the Pyrex reaction vessel being about 3.5 cm. in diameter and 22 cm. long, giving a volume of about 200 cc. Since the qualitative results of Pease⁸ had shown that the reaction started and ended on the walls of the reaction bulb, it was expected that different types or treatment of surface would influence the rate, and therefore particular attention was paid to the construction of the

bulbs used. Five different ones were employed, four of clean Pyrex, and the other of Pyrex coated with potassium chloride. The Pyrex bulbs were cleaned by boiling them in concentrated hydrochloric acid solution for several days, rinsing with distilled water, and were dried by evacuation at 200°. The potassium chloride-coated bulb was prepared by soaking in a concentrated solution of potassium chloride for some days, draining thoroughly, and drying. The deposited potassium chloride was then fused on the surface to ensure a continuous layer. All the bulbs were wrapped in metal foil to exclude light, and all leads were painted with black enamel.

The hydrogen used was prepared by electrolysis of 30% potassium hydroxide on nickel electrodes, purified by passage over heated platinized asbestos, and dried with either calcium chloride or liquid air. It was made fresh for each run and stored in a measuring buret. The chlorine was taken from a tank and led directly into a 1-liter storage bulb. For some experiments this was simply a reservoir from which a desired pressure of chlorine could be obtained in the reaction chamber. In others the chlorine was condensed in this bulb and further purification was attempted by distilling off about a quarter of this at –80°. No difference in the rate of reaction could be traced to this source.

The problem of stopcock grease was a serious one, but it was found that if the stopcocks were protected from light, Apiezon was attacked very slowly and so was satisfactory. None of the peculiar results found could be attributed to the effect of the stopcock grease.

The procedure for making a run was the following. After flushing and evacuating thoroughly, a measured volume of hydrogen was introduced into the reaction bulb from the measuring buret to the desired pressure as given by a quartz spiral manometer, which was used as a null point instrument. Then chlorine was admitted rapidly from the storage vessel up to the desired total pressure, which was again recorded by means of the manometer. After the reaction had proceeded the desired length of time, the gas mixture was admitted successively to two liquid air traps and then to a large Toepler pump. These traps condensed the chlorine and the hydrogen chloride completely as shown by tests. The unreacted and uncondensed hydrogen was pumped by the Toepler back into the measuring buret, where its volume was again meas-

(1) Submitted in partial fulfillment of the degree of Doctor of Philosophy.

(2) Present address: Mallinckrodt Laboratory, Harvard University, Cambridge, Mass.

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

(4) Melander, *Arkiv Kemi, Mineralogi, Geologi*, **5**, no. 12 (1913–1915).

(5) Sachtleben, Dissertation, Hanover, 1914; see Christiansen, ref. 6.

(6) Christiansen, *Z. physik. Chem.*, **B2**, 405 (1929).

(7) Kornfeld and Khodschaian, *ibid.*, **B35**, 403 (1937).

(8) Pease, *THIS JOURNAL*, **56**, 2368 (1934).

ured. The amount of reaction was then determined by difference in hydrogen volumes. The size of the pump and traps was such that all but about 3% of the reacting mixture was removed at the first pump, effectively stopping the reaction at that point.

The reaction bulb was heated by immersion in boiling baths of various organic liquids. For most of the runs an aniline-bath, boiling at 184°, gave a good rate of reaction. Standard runs were one-half atmosphere each of chlorine and hydrogen, for a period of either ten or thirty minutes.

Experimental Data

The results obtained are shown in the tables. Table I is a comparison of absolute rates in the various bulbs used; Table II shows the variation in rate as the reaction proceeds; and Tables III and IV show the kinetic results obtained for the Pyrex 2 and potassium chloride-coated bulbs, respectively.

TABLE I

COMPARISON OF ABSOLUTE RATES						
A. Pure Gases						
Bulb ^a	Mm. H ₂ beg.	Mm. Cl ₂ beg.	Mm. H ₂ end	Mm. Cl ₂ end	Mm. HCl end	Av. rate mm. HCl/min.
Pyrex 1	382	379	275	272	215	7.2
Pyrex 2	399	328	278	208	241	8.0
Pyrex 3	366	419	320	373	92	3.1
Pyrex 4	376	387	324	335	104	3.5
KCl	367	391	306	330	122	4.1

(All runs were for a period of 30 min.)

^a Pyrex bulbs 1 and 2 were cut from the same length of tubing; Pyrex bulbs 3 and 4 from a different length.

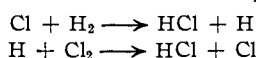
B. With Oxygen Present

	Mm. O ₂	Mm. H ₂ beg.	Mm. Cl ₂ beg.	Mm. H ₂ end	Mm. Cl ₂ end	Mm. HCl end	Av. rate mm. HCl/min.
Pyrex 2	2.3	392	385	361	354	61	0.10
Pyrex 4	1.14	382	372	348	338	67	.11
KCl	2.3	366	390	258	282	217	.36

(Runs were for 600 minutes.)

Discussion of Results

The previous work on the thermal hydrogen-chlorine reaction has shown it quite definitely to be a chain reaction which starts and ends on the walls of the reaction vessel. Additional proof of this will be given in a later paper. Further, the similarity between the thermal and photochemical reaction, particularly with respect to the inhibition by oxygen, makes it seem probable that the Nernst chain is also operating in the thermal reaction. The thermal formation of hydrogen chloride, therefore, undoubtedly proceeds by continued recurrence of the steps



and the major problem is to discover how the chains begin and end.

Before considering processes which may be concerned, attention must be given to the outstand-

TABLE II

1. TIME DEPENDENCE IN PYREX BULBS

Run	Time	Mm. H ₂ beg.	Mm. Cl ₂ beg.	Mm. H ₂ end	Mm. Cl ₂ end	Mm. HCl end	Rate ^a mm. HCl/min.	
A. Pyrex Bulb 1, 184°, Pure Gases								
118	5	381	381	343	343	77	15.4	
117	14	377	391	306	320	141	7.1	
115	30	382	379	275	272	215	4.6	
116	60	382	387	260	265	242	1.5	
121	60	388	377	250	238	278		
119	115	383	384	216	216	336	1.0	
120	323	377	391	147	161	460	0.6	
B. Pyrex Bulb 4, 184°, Pure Gases								
427	10	388	395	353	360	69	6.9	
436	30	385	393	338	346	94	1.2	
428	60	381	385	311	315	140	1.5	
426	120	392	394	288	290	208	1.1	
429	210	390	372	244	226	292	0.93	
Run	Time	Mm. O ₂	Mm. H ₂ beg.	Mm. Cl ₂ beg.	Mm. H ₂ end	Mm. Cl ₂ end	Mm. HCl end	Rate ^a mm. HCl/min.
C. Pyrex Bulb 2, 184°, Oxygen Present								
214	10	1.14	392	394	378	380	28	2.8
216	31	1.14	394	389	377	373	33	0.25
218	90	1.14	395	351	369	325	52	0.32
D. Pyrex Bulb 4, 184°, Oxygen Present								
430	60	1.14	382	395	371	384	21	0.34
431	183	1.14	383	391	367	375	31	.08
432	360	1.14	379	401	354	376	50	.11
433	600	1.14	382	372	348	338	67	.06

2. TIME DEPENDENCE IN KCl-COATED BULB

Run	Time	Mm. H ₂ beg.	Mm. Cl ₂ beg.	Mm. H ₂ end	Mm. Cl ₂ end	Mm. HCl end	Rate ^a mm. HCl/min.
E. Pure Gases, 184°							
K24	15	365	393	322	350	87	6.1
K30	16	373	390	322	339	102	
K26	30	367	391	306	330	122	2.2
K28	30	368	390	304	326	128	
K22	60	367	394	284	311	166	1.8
K23	60	365	391	270	296	189	
K29	60	380	384	287	291	186	1.2
K25	180	376	381	215	220	323	
K21	195	366	390	212	236	307	0.9 ^b
K32	226	375	395	209	229	331	.9 ^b
K31	410	377	389	150	161	455	.67
K27	600	371	394	122	145	498	.17

Run	Temp., °C.	Time	Mm. O ₂	Mm. H ₂ beg.	Mm. Cl ₂ beg.	Mm. H ₂ end	Mm. Cl ₂ end	Mm. HCl end	Rate ^a mm. HCl/min.
F. In Presence of Oxygen									
K76	184	240	2.0	372	379	314	321	116	0.48
K75	184	600	2.0	366	390	258	282	217	0.28
K70	205	30	1.0	386	376	307	297	157	5.2
K71	205	60	1.1	389	370	297	278	184	0.9
K72	205	30	4.0	378	374	334	330	88	2.9
K73	205	240	4.2	403	357	318	272	170	0.4

^a Rates in this table have been computed as the average millimeters per minute of HCl formed since the time of the previous point. This rate calculated from point to point shows the drop in the reaction velocity more clearly than an average rate calculated from the beginning of the reaction.

^b Calculated as average rate from sixty-minute point.

TABLE III
 KINETIC RESULTS IN PYREX 2, 184°

No.	Time	Mm. H ₂ in	Mm. Cl ₂ in	Mm. H ₂ out	Mm. Cl ₂ out	Mm. HCl out	Av. rate mm. HCl/min.	k _A × 10 ⁶
236	10	194	194	155	155	77	7.7	16.0
242	10	195	364	147	316	96	9.6	14.3
239	10	195	452	147	404	97	9.7	12.7
258	10	197	488	159	450	76	7.6	6.7
243	10	396	122	345	71	102	10.2	15.8
246	10	392	185	331	124	122	12.2	10.8
228	10	386	243	309	166	154	15.4	14.6
229	10	386	242	310	166	152	15.2	13.9
259	10	397	391	299	293	196	19.6	14.4
257	10	569	132	517	80	104	10.4	7.1
260	10	569	231	472	134	195	19.5	13.2
232	31	186	85	145	44	81	2.61	20.7
237	30	191	201	134	144	114	3.80	15.3
233	30	190	335	125	270	130	4.33	11.6
238	30	195	420	127	352	135	4.50	8.9
254	30	201	495	140	434	121	4.03	5.2
244	30	396	129	331	64	130	4.33	7.0
245	30	396	171	282	57	228	7.60	25.7
250	30	399	191	294	86	210	7.00	15.2
227	30	386	214	284	112	204	6.80	12.5
249	30	401	223	301	123	200	6.66	8.2
253	30	399	328	278	207	241	8.03	11.2
255	30	561	178	439	56	243	8.10	12.8
235	90	196	191	110	105	172	1.91	18.1
240	91	186	368	96	278	180	1.98	10.3
256	96	197	513	107	423	180	1.88	6.2
247	90	391	185	243	37	295	3.28	21.7
230	90	384	249	218	83	332	3.69	18.2
234	270	193	200	75	81	236	0.87	21.6
241	275	193	376	61	244	263	0.96	13.5
248	322	389	183	208	1	363	1.13	..
231	420	377	235	153	11	448	1.07	14.5

ing feature of the present results: the great decrease in the rate of the reaction as it proceeds. This can be seen clearly by examination of Table II, and is even more evident in Fig. 1, where the total amount reacted is plotted against the time of reaction. The same noteworthy decrease in the rate is observable in the data of every investigator save Melander, and is highly suggestive of an inhibition by the product. However, only Christiansen was able to find an effect by adding hydrogen chloride to the gas mixture, and even his result was considered doubtful. No inhibition by added hydrogen chloride was found in present experiments in the potassium chloride-coated bulb in which hydrogen chloride was allowed to form in the reaction bulb overnight, and then additional reactants were introduced. The same rate was obtained as if no hydrogen chloride were present. With the Pyrex 1 bulb similar experiments showed some inhibition, but not as much as expected.

 TABLE IV
 KINETIC RESULTS IN KCl-COATED BULB AT 184°

No.	Time	Mm. H ₂ in	Mm. Cl ₂ in	Mm. H ₂ out	Mm. Cl ₂ out	Mm. HCl out	Av. rate mm. HCl/min.	k _B × 10 ⁴
K49	15	181	188	162	169	37	2.47	5.36
K37	15	189	399	161	370	57	3.80	5.57
K44	15	194	545	158	509	72	4.80	6.00
K33	16	237	501	201	465	72	4.50	4.70
K41	15	381	176	349	144	65	4.33	4.74
K24	15	365	393	322	349	87	5.80	4.44
K30	16	374	390	323	339	102	6.38	4.82
K47	15	549	234	500	185	98	6.53	4.33
K26	30	367	391	306	330	122	4.07	3.18
K28	30	368	391	304	327	128	4.27	3.37
K48	60	190	183	154	146	73	1.22	2.85
K38	60	188	400	135	347	106	1.77	2.96
K43	60	176	562	110	496	131	2.18	3.43
K35	61	236	508	165	437	143	2.34	2.72
K39	66	380	165	311	96	138	2.09	2.70
K29	60	380	384	287	291	186	3.10	2.54
K23	60	365	391	271	296	189	3.15	2.73
K46	60	549	228	443	122	212	3.53	2.75
K50	165	198	210	115	127	166	1.01	2.58
K36	151	185	427	85	327	199	1.32	2.69
K42	165	182	551	71	441	221	1.34	2.55
K34	150	235	514	111	390	248	1.64	2.37
K40	150	386	156	278	48	217	1.44	1.33
K25	180	376	382	215	220	323	1.70	1.85
K45	155	519	256	357	94	324	2.09	1.91
K32	226	375	395	209	229	331	1.46	1.50
K31	410	377	389	150	161	455	1.11	1.44
K27	600	371	395	122	146	498	0.83	1.22

The only plausible way in which hydrogen chloride could inhibit the chain itself would be to substitute the reaction $H + HCl$ for $H + Cl_2$. But the results of Sommer⁹ show that at 200° the former is only one-sixtieth as rapid as the latter. There are apparently no other species present in the gas phase which might have an inhibiting effect. One is forced to the conclusion that the decrease in rate is caused by some sort of surface action.

The first possibility to suggest itself was that either hydrogen or chlorine standing in the bulb might affect the walls of the vessel in some way which would lessen the rate of reaction. Experiments were performed in which each gas was allowed to stand in the bulb an hour before the other reactant was introduced, but no significant change in the rate occurred.

There remained the possibility that some product of a reaction of both hydrogen and chlorine with the surface was responsible for the decrease in the rate. This product could not be a

(9) Sommer, Dissertation, Berlin, 1934. See Kornfeld and Khodschaian,⁷ also Bodenstein and Winter, *Sitzber. preuss. Akad. Wiss. Physik-math. Klasse*, 2-18 (1936).

permanent coating, since the normal half-hour evacuation between runs was sufficient to restore the bulb to its initial activity, but the chance existed that if one mixture was put in, allowed to react for a time, then pumped out rapidly and another mixture introduced immediately, some of the surface inhibitor might remain and cause the second reaction to be slower. This type of experiment was carried out with the Pyrex 1, Pyrex 4, and the potassium chloride-coated bulbs. The Pyrex 1 bulb showed the expected decrease for the reaction of a mixture introduced in the normal way following quick evacuation, but with the Pyrex 4 bulb a more rapid rate than normal was obtained, and there was no effect at all with the potassium chloride-coated vessel.

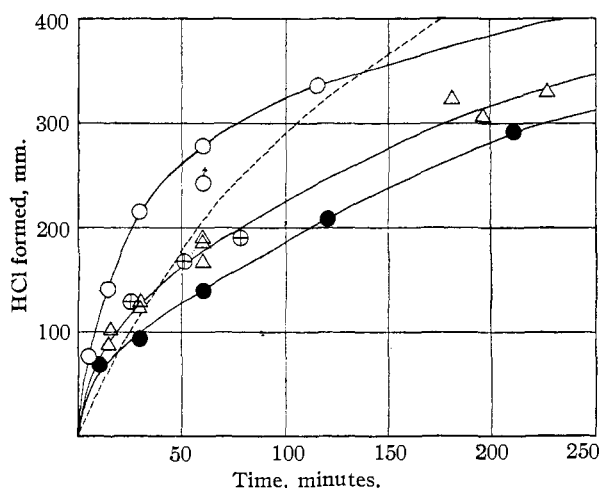


Fig. 1.—Variation in amount of HCl formed with length of time reacting. ○, Pyrex bulb 1; ●, Pyrex bulb 4; △, KCl-coated bulb; ⊕, runs from Pease's table on "Variation of Time," with his times multiplied by a factor of 120 because of temperature difference. The dotted line represents the type of curve which obtains for a simple bimolecular reaction. All curves are for 0.5 atm. each of H_2 and Cl_2 at 184° .

These results were correlated by observing that in each Pyrex bulb the result following the rapid pumping out was the same as that which would have been expected for the initial rate had the surface been covered with potassium chloride. Since the rate in Pyrex 1 was originally faster than in the potassium chloride-coated bulb, the series in that vessel showed a decrease in the rate; since the original rate in Pyrex 4 was slower than in the potassium chloride-coated one, the subsequent reaction proceeded at a faster rate than the standard for that bulb. Apparently as the reaction proceeded a layer of adsorbed hydrogen chloride

or other chloride was formed on the surface of the Pyrex vessel, which altered the rate to that observed with the bulb coated with potassium chloride.

Notice now that the shape of the Time-Amount Reacted curves (Fig. 1) is different for the Pyrex 1 than for the Pyrex 4 and potassium chloride-coated bulbs. In the former the rate shows a continuous decrease, whereas in the latter two there is a short period during which the rate decreases rapidly, following which a steady rate obtains that shows a normal falling off as the reactants are used up. It will be shown in a subsequent paper that this "steady rate" has a special significance, since it is the rate expected if an equilibrium concentration of chlorine atoms were present in the gas phase, and were reacting by the Nernst mechanism. Because this is true and because the "steady rates" in Pyrex 4 and in the potassium chloride-coated bulb are about equal, the initial period should perhaps be regarded as an abnormal acceleration and the slower, steady rate as the normal one for the combination of hydrogen and chlorine. However, it proved just as impossible to find an explanation for an abnormal acceleration as for an inhibition. That the effect was caused by an impurity seems improbable in view of the negative results obtained with all experiments which should have detected such an impurity, and because of the parallel results of other authors.

It should be noted particularly that this effect cannot be attributed to traces of stopcock grease as an impurity, for almost identical curves were obtained by Pease in his results using a flow system where no stopcock grease was present, and a significant decrease is noted in the experiments of Kornfeld and Khodschaian, where special precautions were taken to exclude even traces of such materials.

However, it is possible to determine for both Pyrex and potassium chloride-coated bulbs with which part of the reaction chain the abnormality is associated. If the decrease in rate with time is caused by a changing efficiency of the chain-ending process, then in mixtures containing oxygen the rate curve should become normal. If the apparent inhibition is a part of the starting or propagation of the chains, then the shape should be the same in oxygen-containing mixtures as in pure gases. The results in the presence of oxygen in Table II show that the abnormal shape is

preserved for the potassium chloride-coated vessel, but that in the Pyrex 2 (fast reaction) the curve changes from the type which shows a continuous inhibition to the type observed with pure gases in a potassium chloride-coated bulb. This indicates that the abnormality in the potassium chloride-coated bulb is in the starting or propagation of the chain, but that in the Pyrex 2 bulb the adsorption of the surface inhibitor causes an increase in efficiency of the chain-ending process in pure gases.

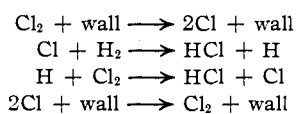
Perhaps there is a connection here with the work of Rodebush and Spealman,¹⁰ who found that hydrogen chloride, apparently that which was adsorbed by the walls of the vessel, was very effective in causing the recombination of hydrogen atoms.

This may also account for the only major discrepancy which still exists in the photochemical hydrogen-chlorine reaction. That is the large inhibition by hydrogen chloride which was found in the seemingly reliable experiments of Norrish and Ritchie,¹¹ and which no other worker has been able to verify. There is much evidence that the chains in the photochemical reaction also end on the walls of the vessel.¹² It may be that Norrish and Ritchie were using a vessel similar to the present Pyrex 2, and that the change in the efficiency of chain stopping at the walls caused an inhibition in their case just as in the present instance. The fact that the inhibition disappeared in the presence of oxygen is confirmation of this. Failure of other authors to observe more than a slight retardation is explained if their bulbs were like the present Pyrex 4 and potassium chloride-coated vessels.

Previous authors, in writing kinetic equations for the hydrogen-chlorine combination, have stressed the dependence of the rate of reaction on the chlorine concentration. None of these equations will fit the present results, either in Pyrex or with the potassium chloride coating, for in both the dependence on hydrogen is much greater than on chlorine.

The results in the potassium chloride-coated bulb lend themselves to a fairly simple interpretation. It has already been noted that the "steady rate" in this bulb corresponds to an equi-

librium concentration of atomic chlorine reacting by a Nernst chain. This suggests a formulation similar to that for the hydrogen-bromine reaction. However, the reaction chains in this case must begin and end on the walls. The effect of the wall, therefore, is simply to catalyze the dissociation and recombination of chlorine molecules. The following series of reactions accords with the above observations.

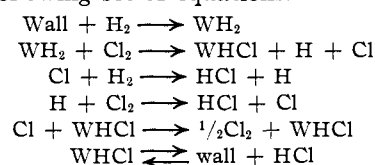


These give the kinetic equation

$$\frac{d^{1/2}\text{HCl}}{dt} = k_B [\text{H}_2][\text{Cl}_2]^{1/2}$$

Constants calculated from the integrated form of this equation are given in the last column of Table IV. While the constants for any given time are fairly good, nevertheless, because of the initial accelerated period, the constants decrease with time. Further, only the part of the reaction which proceeds at the "steady rate" can possibly follow the proposed mechanism. No satisfactory reaction mechanism could be found for the whole course of the reaction.

Qualitatively the kinetic results in Pyrex 2 are like those in the potassium chloride-coated bulb in that there is a high dependence on hydrogen concentration as compared to that on chlorine. Actually, since the absolute rate in Pyrex 2 is much greater than that expected on the basis of an equilibrium concentration of chlorine atoms, the chain starting must be quite different. Nor can it be the same as in the initial accelerated period with the potassium chloride coating, since the two are affected differently by the experiments in which rapid evacuation was resorted to. Further, as will also be shown, the chain-starting in Pyrex 2 (fast reaction) must involve some reaction of hydrogen and chlorine with each other and the wall. Also, in this case there must be provision for the inhibition in the chain-ending process. These requirements are fulfilled in the following set of equations.



This leads, with appropriate assumptions about the nature of WH_2 , to the expression

(10) Rodebush and Spealman, *THIS JOURNAL*, **57**, 1040 (1935).

(11) Norrish and Ritchie, *Proc. Roy. Soc. (London)*, **A140**, 112, 713 (1933).

(12) Semenov, "Chemical Kinetics and Chain Reactions," Oxford University Press, 1935, pp. 95-98.

$$\frac{d^{1/2}[\text{HCl}]}{dt} = k_A \frac{[\text{H}_2]^{1/2}[\text{Cl}_2]}{[\text{HCl}]}$$

which fits the results in Pyrex 2 fairly well. Failure to find the inhibition by hydrogen chloride predicted from this equation for experiments in which some hydrogen chloride was formed in the system previous to the addition of the reactants may be attributed to the interference and counter-influence of an initial accelerated period in the temporarily hydrogen chloride-coated bulb, similar to that found with the potassium chloride-coated vessel. The wide variation in the constants calculated in the last column of Table III is partly caused by the great sensitivity of this equation to small experimental variations.

Further discussion appears in the following paper.

Summary

The thermal reaction between hydrogen and chlorine in clean Pyrex and in Pyrex coated with potassium chloride has been investigated. The

rate of reaction has been shown to depend upon the type of vessel used, and to decrease as the reaction proceeds, in a manner suggestive of inhibition by product, but not attributable to it. A possible explanation for the inhibition in clean Pyrex has been suggested.

Different kinetic equations were found necessary for the reaction in clean glass and in glass coated with potassium chloride. In the coated bulb the results could be best interpreted by means of the equation:

$$\frac{d^{1/2}[\text{HCl}]}{dt} = k_B [\text{H}_2][\text{Cl}_2]^{1/2}$$

whereas for clean Pyrex the expression

$$\frac{d^{1/2}[\text{HCl}]}{dt} = k_A \frac{[\text{H}_2]^{1/2}[\text{Cl}_2]}{[\text{HCl}]}$$

was developed in an attempt to correlate the data. These equations differ somewhat from those of previous authors.

PRINCETON, N. J.

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The Thermal Hydrogen-Chlorine Reaction. II. Relation to the Theory of Chain Reactions¹

BY J. C. MORRIS² AND R. N. PEASE

In a previous paper³ experimental data on the thermal reaction between hydrogen and chlorine were presented. In this paper an attempt will be made to correlate the data with those of other workers and to explore resulting theoretical implications.

The chain character of this reaction may be considered definitely established. The inhibition by oxygen, the lack of acceleration with packing, the calculations of Eyring⁴ have all shown a chain mechanism to be the most probable. Along with this, experiments and calculations have tended to show that the chains start and end on the walls of the reaction vessel. Further evidence to support this will be considered later. It will be assumed also that the chain which is operating is the Nernst chain.

Some general principles of chain processes

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(3) Morris and Pease, *THIS JOURNAL*, **61**, 391 (1939).

(4) Eyring, *ibid.*, **53**, 2537 (1931).

which are applicable to the hydrogen-chlorine reaction are worthy of consideration. For example there are very definite limits to the absolute rate of such reactions. Suppose that, as in the case of $\text{H}_2 + \text{Br}_2$, the chains in the present case are started by a thermal gas phase dissociation of chlorine molecules and ended by a recombination of the atoms. Then, whatever the reactions in the body of the chain may be, the steady-state concentration of chlorine atoms will be equal to the thermal equilibrium concentration in a similar system where no reaction is occurring, and the rate of formation of hydrogen chloride will be equal to the rate at which this concentration of atomic chlorine interacts with hydrogen, multiplied in this case by two. Since the dissociation equilibrium of chlorine and the activation energy of the reaction are known, one can calculate the rate of formation of hydrogen chloride if these chain-starting and -ending processes prevail.

Now if another chain-ending reaction is to be