mately 2.24 Å., an important one at 3.55 Å., a third at 5.18 Å. and a fourth at 6.9 Å. The first peak may be attributed to the unresolved C–I and C–C distances, both of which should appear to a smaller extent than I–I distances. Thus it appears that the shortest distance between iodine atoms is 3.55 Å. The electronic structure of the covalent molecule would be similar to that of the triiodide ion, in that both require ten electrons to be assigned to an iodine atom. The I–I distance in ammonium triiodide is 2.8 Å.,[2] and the sum of the covalent radii of the atoms is 2.7 Å.;[3] we would hence expect to find the iodine–iodine distance in diphenyliodonium iodide to be 2.7–2.8 Å. if the bond were covalent. Thus we see that the covalent structure cannot be the correct one. On the other hand, the experimental value of 3.55 Å. is compatible with an ionic structure; the shortest distance between iodine atoms in different molecules in crystalline I_2, with each atom forming one covalent bond, is 3.54 Å., and we would expect a similar distance between an iodonium ion with two covalent bonds and an iodide ion with no covalent bonds.

I am indebted to Mr. E. R. Kennedy for preparing the sample, and to Professor Linus Pauling, who has contributed many suggestions.

PASADENA, CALIF. RECEIVED APRIL 8, 1935

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[2] Mooney, *Phys. Rev.*, **45**, 755 (1934).

[3] Pauling and Huggins, *Z. Krist.*, [A] **87**, 205 (1934).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photosynthesis of Hydrogen Chloride

BY J. C. POTTS AND G. K. ROLLEFSON

The photochemical reaction between hydrogen and chlorine has been the subject of numerous investigations in which a wide variety of results has been obtained. The early work was complicated by a failure to work with pure hydrogen and pure chlorine, but even the two most recent investigations show a marked disagreement.[1] The rate laws which have been given are

$$\frac{\mathrm{d(HCl)}}{\mathrm{d}t} = kI_{\mathrm{abs.}}\,(\mathrm{H_2}) \qquad \text{(Bodenstein and Unger)}$$

$$\frac{\mathrm{d(HCl)}}{\mathrm{d}t} = \frac{kI^{0.6}_{\mathrm{abs.}}\,({}_2\mathrm{H})}{1 + k'\,(\mathrm{HCl})/(\mathrm{Cl_2})} \qquad \text{(Derived from a formula for } \gamma \text{ given by Norrish and Ritchie)}$$

The effect of extreme drying reported by Coehn and Jung[2] has been shown to be non-existent.[3]

In this paper we are reporting the results of a series of experiments designed to test these rate laws. Most of our results are essentially in agreement with Bodenstein and Unger but we have also succeeded in finding conditions under which the $I^{1/2}_{\mathrm{abs.}}$ law is obeyed.

Experiments have been performed at various temperatures from 140 to 300°K. The apparatus shown in Fig. 1 was used in the lowest part of this temperature range. The reaction vessel (A) was enclosed in the lead radiation shield (B). A stream of cold air, prepared by bubbling dry air through liquid air contained in the space (C) between the bottom of the lead block and the Dewar (D), flowed along the sides of the block (B) and kept it from warming up. A tube (E) provided a means of directing a jet of liquid air directly on the lead block for rapid cooling and a second tube (F) permitted the introduction of liquid air directly into (C). Several sections of copper wire, each 61 meters long (not shown in the figure) wound around the block and the reaction vessel were used both as resistance thermometers and as heating coils. G was a Pyrex window fitted into the lead block. By careful manipulation of this apparatus the temperature could easily be kept constant to better than 0.1°.

In the experiments with this apparatus solid or liquid chlorine was always present, so the reaction could be followed by observing the pressure change; in a few experiments the chlorine and hydrogen chloride were frozen out and the residual hydrogen measured.

For temperatures from 200 to 273°K. the reaction vessel was immersed in a bath of cold methyl alcohol contained in a transparent Dewar flask. At 273°K. and above, water was used instead of methyl alcohol. In these experiments the reaction was followed by removing the water or alcohol

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[1] Bodenstein and Unger, *Z. physik. Chem.*, **B11**, 253 (1930); Norrish and Ritchie, *Proc. Roy. Soc.* (London), **A140**, 112 (1933).

[2] Coehn and Jung, *Z. physik. Chem.*, **110**, 705 (1924).

[3] Allmand and Craggs, *Nature*, **130**, 927 (1932); Rollefson and Potts, THIS JOURNAL, **55**, 860 (1933); Bernreuther and Bodenstein, *Sitzungsber. preuss. Akad.*, 6 (1933); Rodebush and Klingelhoefer, *Proc. Nat. Acad. Sci.*, **18**, 531 (1932).

bath and substituting one of liquid air (in some experiments liquid oxygen was used), thus freezing out the chlorine and hydrogen chloride, and observing the pressure of the residual hydrogen. Pressures were measured by means of sulfuric acid manometers. Numerous tests have shown that these do not introduce any disturbing effects.

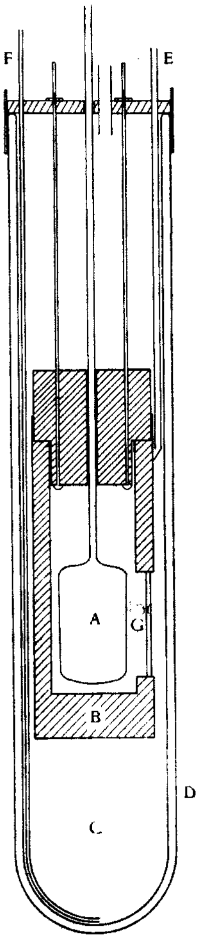

Fig. 1.—Reaction vessel and thermostat for rate measurements at low temperatures.

The hydrogen was prepared by electrolysis; it was passed over hot, finely divided copper to remove oxygen, and dried by passing it through a trap set in liquid air.

The chlorine was prepared by decomposing anhydrous cupric chloride.

The hydrogen chloride was prepared by dehydrating C. P. hydrochloric acid with concentrated sulfuric acid. The gas was bubbled through concentrated sulfuric acid. It was then frozen out with liquid air, the first and last fractions were discarded, and the middle portion was stored in a Pyrex bulb.

Our experimental results are divided into two groups: those obtained at temperatures below 172°K. (the melting point of chlorine), and those above 200°K. No useful results were obtained between 172 and 200°K. as in that region the mutual solubility of hydrogen chloride and chlorine made the composition of the gas phase uncertain; at higher temperatures no liquid was present. The most striking difference between the two regions is in the rate law. The light absorbed appears to the first power at the higher temperatures and to the one-half power in the lower range. At all temperatures the hydrogen pressure enters to the first power. For the low temperature range this is demonstrated by the data given in Table I. Unless specifically stated in the text, data in different tables are not to be compared; the experiments were performed at intervals during a period of several years with a number of different experimental arrangements.

TABLE I

EFFECT OF VARYING HYDROGEN PRESSURE AT CONSTANT LIGHT ABSORBED, TEMP. 167°K.

Time, min.	(H_2) pressure, cm. of sulfuric acid	Log(H_2)	Time, min.	(H_2) pressure, cm. of sulfuric acid	Log(H_2)
0	42.0	1.623	27	31.1	1.493
2	41.4	1.617	30	30.0	1.477
4	40.5	1.608	35	28.0	1.446
6	39.6	1.598	40	26.4	1.422
8	38.7	1.588	45	24.8	1.395
10	37.8	1.578	50	23.4	1.369
12	36.9	1.569	55	21.9	1.339
15	35.6	1.551	60	20.6	1.314
19.5	33.9	1.530	65	19.3	1.286
21	35.6	1.526	70	18.2	1.259
24	32.2	1.507	75	17.1	1.232

The effect of varying the incident light intensity in the same temperature range is shown by the data in Table II.[4] Data such as presented in Table II may be tested by plotting against what we have called the "reduced time." By "reduced time" we mean that the actual time intervals have been multiplied by the light intensity raised to the power which is being tested. The application of this method to the data in Table II is shown in Fig. 2, which shows very clearly the validity of the square root law.

TABLE II

EFFECT OF VARYING THE INCIDENT LIGHT INTENSITY

Temp. 167°K. Solid chlorine and liquid hydrogen chloride present. Hydrogen pressure measured at liquid air temperature.

Light intensity	Reduced time, min. I^0	$I^{1/2}$	I^1	$P(H_2)$	Log (H_2)
	0	0	0	26.49	1.424
0.32	100	57	32	25.00	1.398
1.00	160	117	92	23.60	1.372
1.00	220	177	152	22.10	1.344
0.32	325	237	185	20.91	1.320
1.00	385	297	245	19.43	1.289
0.148	541	357	268	18.19	1.260

At temperatures around 273 to 300°K. the rate is dependent on the first power of the light absorbed and of the hydrogen. As the fraction of the incident light absorbed is always small, we may make the substitution $I_{\text{abs.}} = I_0(Cl_2)$ and write the rate law

$$d(HCl)/dt = kI_0(Cl_2)(H_2)$$

The general validity of this law is shown in Fig. 3 where use is made of the integrated form of this equation. By plotting $[1/(Cl_2) - (H_2)]$ log $(Cl_2)/(H_2)$ against time, kI_0 is proportional to the

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(4) Since the fraction of light absorbed is always small $I_{\text{abs.}} \propto I_0$. A set of calibrated screens was used to vary the incident light intensity.

slope. It is apparent that there is no detectable induction period and the lines are approximately straight. Closer examination reveals a slight falling off in kI_0 although it is far smaller than the effect called for by Norrish's equation. The general magnitude of this effect is shown by the data in Table III which also involve changes in I_0.

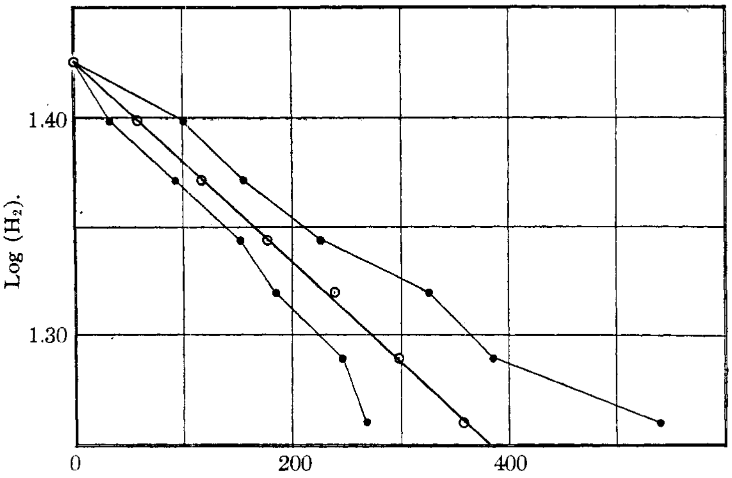

Fig. 2.—Test of the effect of varying the light intensity. Temperature 167°K.

TABLE III

The hydrogen pressures are those read with the reaction vessel immersed in liquid air; the chlorine pressures have been reduced to corresponding units. $k = [\Delta \log(Cl_2)/(H_2)]/I_0t$.

Run A

Time	I_0	$p(H_2)$	$p(Cl_2)$	Log $(Cl_2)/(H_2)$	k
0		12.55	15.67	0.0965	
1	1.00	9.75	12.87	.1206	0.0241
2	1.00	8.00	11.12	.1430	.0224
5	0.148	7.51	10.63	.1509	.0156
8	.148	7.05	10.17	.1590	.0182
9	1.00	6.20	9.32	.1770	.0180
11	1.00	4.97	8.09	.2115	.0172

Run B

Time	I_0	$p(H_2)$	$p(Cl_2)$	Log $(Cl_2)/(H_2)$	k
0		11.65	15.75	0.1309	
1	1.00	9.75	13.85	.1525	0.0216
3	0.379	8.71	12.81	.1675	.0198
4	1.00	7.60	11.70	.1874	.0199
6	0.379	7.00	11.10	.2002	.0169
8	1.00	5.80	9.90	.2322	.0160

These experiments show definitely that the rate is dependent on the first power of the intensity of the incident light. We are therefore in essential agreement with the results of Bodenstein and Unger; but our results show a gradual decrease in k throughout the run instead of the erratic variations observed by them. This decrease is due to three distinct factors which are difficult to separate: (1) an inhibiting effect by the hydrogen chloride formed; (2) production of a substance other than hydrogen chloride which inhibits the reaction (probably formation of a silicon chloride); (3) the average temperature of the reacting mixture is above that of the thermostat surrounding the reaction vessel, as is shown by the Draper effect. This temperature difference decreases during the course of the reaction and causes a corresponding decrease in k. If we attempt to eliminate this third effect by reducing I_0, the second effect becomes more important, so that but little advantage is gained. Since these three effects are in the same direction we are able to give only an upper limit to the magnitude of the hydrogen chloride effect, but not to obtain accurate measurements of it. Regardless of what other steps may be assumed, if we limit the action of hydrogen chloride to

$$H + HCl = H_2 + Cl$$

and that of atomic hydrogen to this reaction and

$$H + Cl_2 = HCl + Cl$$

then the inhibiting action of hydrogen chloride introduces the factor $1/[1 + k'[(HCl)/(Cl_2)]]$ into the rate law. According to Norrish and Ritchie $k' = 1.7$, which is obviously much too high to agree with our data (illustrated in Fig. 3). Our experiments do not permit a very exact

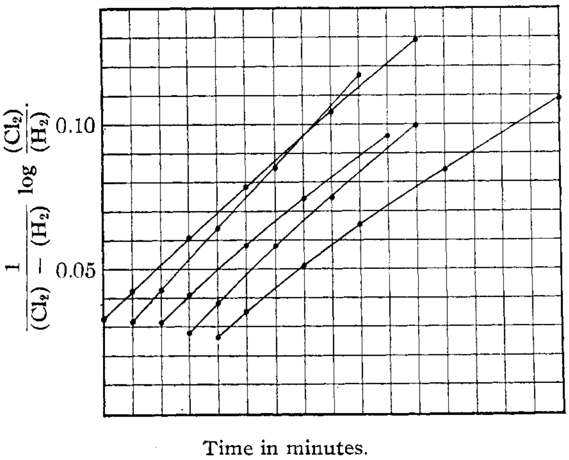

Fig. 3.—Reactions at 273°K. In order to separate the runs the time zeros have been shifted so as to separate the initial points by one minute on the plot.

calculation of k' but they indicate that the upper limit is probably about 0.1. Norrish and Ritchie attributed the failure of Bodenstein and Unger to observe an inhibiting effect by hydrogen chloride to the fact that in their experiments as the hydrogen chloride pressure increased the hydrogen pressure decreased; this would offset the hydrogen chloride effect if hydrogen were also an inhibitor. Table IV shows the composition of the reaction mixture and initial values of kI_0 for a number of our experiments. It is evident that hydrogen is not the inhibitor it would have to be to fit the explanation given by Norrish and Ritchie.

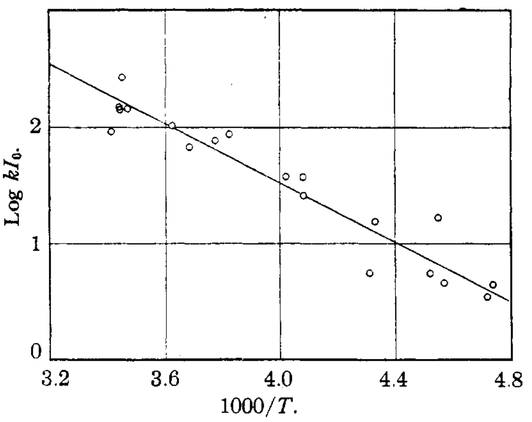

Fig. 4.—Effect of temperature on the rate law, $d(HCl)/dt = kI_0(H_2)(Cl_2)$.

Table IV

H_2	Cl_2	KI'_0
13.18	12.90	111
14.84	12.65	92
14.90	11.67	96
17.70	10.25	113
20.10	8.90	99
18.50	12.95	104
17.05	16.05	88
11.17	19.60	119
		Av. 103

We may summarize our conclusions from rate measurements by two equations. The first

$$\frac{d(HCl)}{dt} = kI_{abs.}(H_2)\frac{1}{1 + k'[(HCl)/(Cl_2)]} \qquad k' \leq 0.1$$

which holds at ordinary temperatures and down to approximately 200°K. The second

$$\frac{d(HCl)}{dt} = k_1 I^{1/2}_{abs.}(H_2)$$

holds for temperatures below the melting point of chlorine (172°K.). The omission of the factor $1/[1 + k'(HCl)/(Cl_2)]$ at low temperatures is due to our failure to detect such an effect. The experimental conditions which may be used to test such an effect are limited by the condensation of hydrogen chloride when attempts are made to obtain a high value for the $(HCl)/(Cl_2)$ ratio. We would say that k' in that factor is certainly not greater than 0.1 at the low temperatures and is probably much less.

Another slight difference in behavior of the system in the two regions is found in the temperature coefficients of k and k_1. These are most readily obtained in experiments using light of wave length approximately 3600 Å., as the absorption coefficient of chlorine is practically independent of temperature at such frequencies. The data for k are plotted in Fig. 4 and give a slope corresponding to a heat of activation of 5.8 kcal., which is in unusually good agreement with the value 5.88 kcal. calculated from Hertel's data[5] on oxygen-free reaction mixtures.

Figure 5 shows the data for low temperatures. We have plotted d $\log(H_2)/dt$ against $1/T$ in this figure; therefore, in order to get the heat of activation corresponding to k_1, it is necessary to subtract one-half the heat of vaporization of chlorine from the heat calculated from the plotted data. The final result is 4.6 kcal., which is definitely lower than the value obtained at higher temperatures. (If chlorine enters the rate law other than in $I^{1/2}_{abs.}$ this activation energy must be decreased more.)

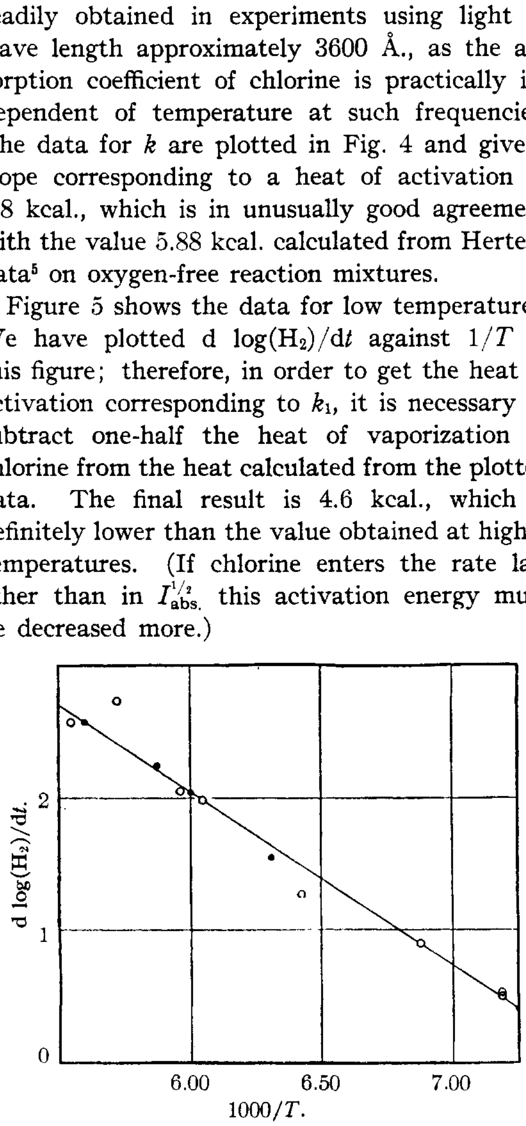

Fig. 5.—Effect of temperature on the rate law $d(HCl)/dt = k_1 I^{1/2}_{abs.}(H_2)$. The circles represent data taken in 1932 and the dots data taken in 1934.

The change in the exponent of $I_{abs.}$ may be explained most readily from a mechanism standpoint by assuming that under one set of conditions

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[5] Hertel, *Z. physik. Chem.*, **B15**, 325 (1931).

the chlorine atoms are destroyed by recombination in the gas phase and under the other conditions they are destroyed either at the wall or by reaction with some gaseous impurity. Bodenstein and Unger have given an extensive discussion of the possibility of the chains terminating at the walls: they prefer a mechanism involving removal of chlorine atoms by a substance X which they believe is a chloride or oxychloride of silicon formed by the action of chlorine atoms or hydrogen chloride on the silica in the walls of the reaction vessel. Our observations with experimental conditions similar to theirs are in complete agreement with these statements. The fact that merely lowering the temperature changes the power of light absorbed in the rate law from one to one-half is strong evidence for the removal of chlorine atoms by some volatile substance. Estimates of the vapor pressures of various possible impurities (such as silicon tetrachloride) indicate that at temperatures below 172°K. their concentrations would be too low to affect the reaction.[6]

We have performed a number of experiments in an attempt to locate the source of the large inhibiting effect attributed by Norrish and Ritchie to hydrogen chloride. Some typical results are given in Table V.

TABLE V

Time	p_{H_2}	p_{Cl_2}	p_{HCl}	Rate
0	14.1	13.8	36.9	
0.5	14.0	13.7	37.1	0.210
1.5	13.8	13.5	37.5	
3	13.5	13.2	38.0	0.168
6	13.1	12.8	38.9	.155
13	12.0	11.7	41.0	.122
20	11.3	11.0	42.4	.105
30	10.3	10.0	44.5	.085
45	9.2	8.9	46.6	.060
60	8.5	8.2	48.1	.044
0	15.5	15.5	18.0	0.560
1	14.9	14.9	19.2	.491
2.5	14.3	14.3	20.4	.426
5	13.3	13.3	22.3	.344
9	12.1	12.1	24.7	.270
15	10.7	10.7	27.6	.192
25	9.20	9.20	30.5	.124
40	7.7	7.7	33.5	.085
50	7.0	7.0	35.0	.071

If we compare the initial rates of the two experiments we find a large inhibiting effect due to the hydrogen chloride added ($k' = 3$, in fair agreement with Norrish and Ritchie). However, if we examine the effect of the increasing $(HCl)/(Cl_2)$ ratio during the run we obtain $k' = 0.1$, approximately. This indicates that the large inhibition is due to some impurity introduced with the hydrogen chloride rather than to hydrogen chloride itself. This discrepancy would have been missed if initial rates alone had been observed, as was true in the work of Norrish and Ritchie. Therefore we believe that in spite of all the precautions taken by the latter they introduced some inhibitor with their hydrogen chloride which accounted for the results reported.

In addition to our experimental results opposed to the inclusion of a large inhibition attributed to the $(HCl)/(Cl_2)$ ratio there are definite theoretical objections. It is generally conceded that the specific reaction rate for $H + Cl_2 = HCl + Cl$ is at least one hundred times as large as for $Cl + H_2 = HCl + H$. The inhibiting action of hydrogen chloride is attributed to the reverse of the latter reaction and Norrish and Ritchie give this a specific reaction rate 1.7 times that for the reaction between atomic hydrogen and chlorine which leads to a value for the equilibrium constant $(HCl)(H)/(Cl)(H_2) = 0.0059$. This constant may also be calculated from thermodynamic data. The heat of dissociation of hydrogen is 102,300 cal. and of chlorine 57,000 cal. The heat of formation of hydrogen chloride is 22,775 cal. and the entropy change for the reaction $Cl + H_2 = HCl + H$ is 23.62 E. U. The equilibrium constant calculated from these data is 1.5. The only quantity involved in these calculations which may be considered at all uncertain is the heat of dissociation of hydrogen; if we repeat the calculations using 99,300 and 105,300 cal., which are probably the extreme limits, we find 18.5 and 0.12, respectively. Even the lowest of these values is twenty times the one required to fit the data given by Norrish and Ritchie.

Summary

Experiments have been carried out over a wide range of conditions in order to test the validity of the rate laws for the photochemical formation of hydrogen chloride which have been given by Bodenstein and Unger and by Norrish

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[6] If the concentrations of these impurities could be reduced to this extent at room temperature we should expect to find the square root of the light absorbed in the rate law. Under such conditions the quantum yield should be very much higher than was observed by Bodenstein and Unger. Norrish and Ritchie obtained quantum yields of the same magnitude as Bodenstein and Unger, which excludes the possibility of their gases having the necessary degree of purity.

and Ritchie. At ordinary temperature the results are in agreement with the equation of Bodenstein and Unger, except that a small correction must be made for an inhibiting action by the hydrogen chloride formed. At temperatures below 172°K. the rate depends on the square root of the light absorbed instead of the first power. The temperature coefficient of the reaction has been determined both at ordinary and at low temperatures. The discussion includes a possible explanation for the change in the rate law as the temperature is lowered and some comments on the work of Norrish and Ritchie.

BERKELEY, CALIF. RECEIVED APRIL 8, 1935

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, AND FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Polymerization of Deutero-acetylene by Alpha-Rays[1]

BY S. C. LIND,[2] J. C. JUNGERS[3] AND C. H. SCHIFLETT[4]

Introduction.—It is well known that acetylene under the influence of alpha-radiation from radon mixed with the gas polymerizes to a solid known as cuprene.[5] Preliminary experiments showed that a similar solid was obtained when deutero-acetylene was subjected to the rays. The $-M/N$ (the number of molecules of acetylene polymerized per ion pair) for ordinary acetylene is approximately twenty.[6] It was of interest, therefore, to know this value for deutero-acetylene. In this paper are reported the results of the direct determination of $-M/N$ and also the results of a more exact comparison of the reaction rates of the polymerization of heavy and light acetylene by a pressure differential method.

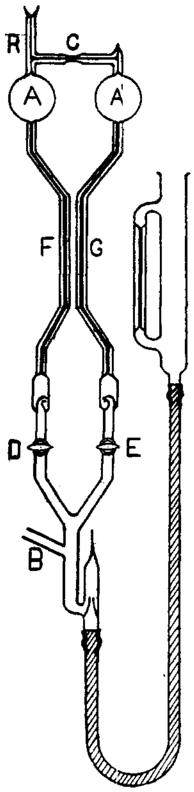

Fig. 1.

Experimental Procedure.—The direct determination of $-M/N$ for deutero-acetylene was made in the usual way[5,6] and found to agree[7] with the value previously obtained for ordinary acetylene within 5%. The following method was devised to permit of a more critical comparison of the rates of polymerization. Radon was introduced into A and A′ (Fig. 1) through R, after which the system was sealed off at R. Care was taken to have reaction vessels A and A′ as nearly the same volume as reasonably possible so that the radon might distribute itself equally between the two vessels. Several hours were then allowed to elapse, after which the connecting capillary was sealed at C. Deutero-acetylene was then introduced into A through B and D and ordinary acetylene into A′ through B and E. For the purpose of this comparison it was important to adjust the pressure of C_2H_2 in A′ quickly to equal within a few millimeters that of C_2D_2 in A so that the mercury levels in the parallel tubes at F and G could be read at one major setting of the leveling bulb and cathetometer. The reactions were then followed manometrically. The equality of distribution of radon between the two vessels, which was checked by gamma-ray comparison by shielding from the electroscope first one and then the other bulb with lead, was found to be satisfactory.

Preparation of Acetylenes

Preparation of Deutero-acetylene.—Some difficulty has been experienced in the preparation of pure deutero-acetylene free from contamination with hydrogen (ordinary).[8] Accordingly, the following method was adopted. A (Fig. 2) is the vessel destined to receive the acetylene; B and D are traps. E is a small volume containing pure D_2O. C is the vessel containing calcium carbide. After the whole was carefully dried, the stopcocks were greased and put in place and the calcium carbide was dropped into

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(2) Director of the School of Chemistry, University of Minnesota.

(3) C. R. B. Fellow.

(4) Assistant Professor of Chemistry, Macalester College, St. Paul, Minnesota.

(5) Mund and Koch, *Bull. soc. chim. Belg.*, **34**, 125 (1925); Lind and Bardwell, *Science*, **62**, 423 (1925).

(6) Lind, Bardwell and Perry, THIS JOURNAL, **48**, 1558 (1926); Mund and Koch, *J. Phys. Chem.*, **30**, 293 (1926).

(7) *Phys. Rev.*, **46**, 825 (1934).

(8) McKellar and Bradley, *Phys. Rev.*, **46**, 664 (1934).