the more dilute sucrose solution is probably due largely to the greater amount of potassium acid tartrate soluble in a 20% solution as compared with a 50% sucrose solution. These results, while they indicate that a slow inversion of sucrose no doubt takes place which would be completed over a long time period and affect the solubility data, show that the correction is of too small magnitude to be considered as a factor in attaining solubility equilibrium in our work.

From the data it appears that the solubility of potassium acid tartrate decreases in the presence of sugars as the concentration of the latter is increased. Arranged in their order of increasing effectiveness in reducing the solubility of the acid tartrate, the sugars take the order *d*-fructose, invert sugar, *d*-glucose and sucrose.

It was of interest to calculate the solubility of potassium acid tartrate in the various sugar solutions to a common basis such as the water basis, to note any solubility effect due to the nature of the sugar. It was found that *d*-fructose, invert sugar and *d*-glucose increased the solubility of acid tartrate (on a fixed water basis) as the sugar content was increased, the first mentioned having the greater effect. On the other hand, the sucrose concentration had little effect on the amount of acid tartrate dissolved in a fixed weight of water. We are inclined to attribute this effect to the presence of the highly reactive ketone group in *d*-fructose, while the aldehyde group in *d*-glucose is presumably less reactive, and the respective groups in sucrose are inactive due to internal linking within the disaccharide molecule.

Summary

1. The solubility of potassium acid tartrate in solutions of *d*-glucose, *d*-fructose, invert sugar and sucrose has been determined for a series of sugar concentrations at 0, 5, 10, 15 and 20°.

2. The solubility of the acid tartrate in the various sugar solutions at various concentrations may be expressed by the general equation $C_{\mathrm{KHT}} = K - kC^a_{\mathrm{Sugar}}$, in which C_{KHT} and C_{Sugar} represent the concentration in milligrams per 100 g. of solution, respectively, of potassium acid tartrate and of the sugar under consideration. K represents the solubility of the acid tartrate in water and k and a are constants which depend on the temperature and the kind of sugar.

3. The solubility of potassium acid tartrate decreases in the presence of sugars as the concentration of the latter is increased. Arranged in their order of increasing effectiveness in reducing the solubility of the acid tartrate, the sugars take the order, *d*-fructose, invert sugar, *d*-glucose and sucrose.

4. When calculated on the basis of a fixed amount of water as solvent, it has been found that the solubility of potassium acid tartrate is noticeably increased by increasing concentrations of *d*-fructose, invert sugar and *d*-glucose but is practically unchanged by increasing concentrations of sucrose.

GENEVA, N. Y. RECEIVED SEPTEMBER 15, 1933

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

The Role of Oxygen as an Inhibitor for the Photosynthesis of Hydrogen Chloride

BY K. B. KRAUSKOPF AND G. K. ROLLEFSON

When a mixture of H_2, O_2 and Cl_2 is illuminated with light absorbed by Cl_2, part of the H_2 combines with Cl_2 and part with O_2. The relative amounts of HCl and H_2O formed depend on the O_2/Cl_2 ratio. An investigation of the amounts formed when this ratio is large affords a direct means of determining whether the well-known inhibiting effect of O_2 on the HCl reaction is due to a reaction with H atoms or to a reaction with Cl atoms.

Thus, suppose that the initial pressure of O_2 is increased rapidly in successive runs. If a reaction between O_2 and Cl occurs to any great extent, the amount of HCl formed should fall off regularly until finally the Nernst chains fail to start at all. On the other hand, if a reaction between O_2 and H predominates, HCl production can never fall to zero, but should approach some small limiting value, since the formation of an H atom requires the simultaneous production of an HCl molecule. Water formation in the first case should eventually become much larger than HCl formation, but in either case should remain small.

In the present work a study of the relative amounts of HCl and H_2O produced has been carried out for O_2/Cl_2 ratios up to 100/1. The results are in agreement with similar experiments reported very recently by Chapman and Watkins,[1] and corroborate conclusions reached from entirely different considerations in two other recent papers.[2,3] O_2 inhibition is due chiefly to a reaction with H atoms.

Apparatus and Materials

A cylindrical Pyrex reaction vessel of about 150 cc. capacity was used, connected by capillary tubing to a mercury manometer. The manometer was U-shaped, about 150 cm. high, with one side evacuated, so that total pressures up to two atmospheres could be used. To protect the mercury surface from chlorine a layer of sulfuric acid was used. The protection was not complete, however, and it was necessary to clean the manometer after every five or six runs.

The light source was a Cooper–Hewitt mercury arc, operating on a 110-volt line. High light intensities were needed, so the arc was placed close to the reaction vessel and its light was focused with a cylindrical lens.

Oxygen was obtained from commercial tanks. It was liquefied with liquid air and distilled, only the middle fraction of a large quantity being kept. The gas was dried and stored over anhydrone. Doubtless a trace of nitrogen remained with the oxygen after this treatment, but greater purity was unnecessary.

Hydrogen was obtained by electrolysis of a solution of potassium hydroxide. It was passed over hot copper, and carefully dried by passing it slowly through a quantity of anhydrone. The gas was stored in contact with anhydrone.

Chlorine was obtained by heating copper chloride.[4] The copper chloride, thoroughly dehydrated by long heating and finally heated strongly under a vacuum, was placed in a tube connected directly to the reaction vessel. Thus chlorine could come in contact with stopcock grease only at the one stopcock which served for the admission of other gases and for evacuating the reaction vessel.

Hydrogen chloride was prepared from hydrochloric acid and concentrated sulfuric acid. It was frozen with liquid air, distilled and dried over anhydrone.

Experimental Procedure

Before each run gases from the preceding run were removed by evacuating the reaction vessel and flushing it with oxygen. Traces of material from a preceding run had no noticeable effect on the reaction, so great care in flushing the system was unnecessary.

In each run chlorine was the first gas admitted to the reaction vessel, but to protect the manometer a little oxygen was usually present while the copper chloride was heated. Oxygen and hydrogen were then admitted from their storage bulbs; it was often convenient to admit them while the reaction vessel was immersed in liquid oxygen. All gas pressures either were read while the reaction vessel was kept at 25° or were read at the temperature of liquid oxygen and converted to 25° by an appropriate factor.

The rates of both hydrogen chloride formation and water formation were affected only very slightly by temperature changes, so no special precautions were taken to ensure uniform temperatures during the periods of illumination. The majority of runs were made at about 25° with the reaction vessel exposed to the air; fluctuations of the manometer indicated temperature variations sometimes up to three or four degrees. In the runs at 0° the temperature variation was much less, since the reaction vessel was placed in an unsilvered Dewar flask filled with ice and water. Temperatures around 85° were maintained simply by varying the resistance in series with a knife heater, so for these runs the temperature fluctuation was usually two or three degrees.

After each period of illumination in all runs, two readings were taken, one while the reaction vessel was held at 25° and another while it was immersed in liquid oxygen. The presence of sulfuric acid in the manometer caused some difficulty in making the readings, since it was necessary to have the same amount of acid on top of the mercury for consecutive readings in each run.

The formation of HCl from H_2 and Cl_2 involves no pressure change at room temperatures, but at the temperature of liquid oxygen, where both Cl_2 and HCl are solids, the progress of the reaction can be followed by observing the decrease in H_2 pressure. The rate of production of H_2O can be found from the readings at 25°, since this reaction involves a pressure change at room temperatures. The actual calculation from a given pair of readings of the amounts of HCl and H_2O formed is somewhat complicated because of the condensation of water and the solution of some HCl in the condensed water.

Briefly, the calculation may be described as follows. A rough estimate of the amount of gaseous HCl present is made from previous readings and from comparison with other runs. This pressure of HCl determines the concentration of the solution of HCl in the condensed water. Fortunately the solutions encountered in these runs are so concentrated that variation of the concentration with the pressure of HCl is small, and accordingly an estimate of the HCl pressure determines the molality with fair accuracy. The vapor pressure of H_2O over a solution of this molality, *i. e.*, the amount of water present in the gas phase, can be found from tables. Now the total pressure change at 25°, $\Delta_{p25°}$, is made up of three parts: $\Delta p_{25°}$ = change due to disappearance of H_2 and O_2 in liquid H_2O + change due to disappearance of H_2 and O_2 in gaseous H_2O + change due to solution of HCl in liquid H_2O. Of these three quantities the second is found as described above. The third may be expressed in terms of the amount of liquid H_2O present and the estimated pressure of HCl. If these substitutions are made in the formula for $\Delta p_{25°}$, the equation can be solved for the total amount of water formed in terms of the measured quantity $\Delta p_{25°}$ and the estimated pressure of HCl. As stated above, variation with this estimated quantity is small, so that an approximate value is usually sufficient. If the true value for the HCl pres-

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(1) Chapman and Watkins, *J. Chem. Soc.*, 743 (1933).

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

(3) Bodenstein and Schenk, *Z. physik. Chem.*, **B20**, 420 (1933).

(4) Rollefson, THIS JOURNAL, **51**, 770 (1929); Loeb, *Phys. Rev.*, **35**, 184 (1930).

sure, found as indicated in the next paragraph, turns out too greatly different from the estimated value, a second approximation can be made with this more correct figure.

When the amount of H_2 used in H_2O formation has been found, the amount used in HCl formation may be obtained directly from the pressure change at −180°, $\Delta p_{-180°}$. The formula is most concisely written

$$H_2 \text{ used in HCl} = g\,\Delta p_{-180°} - {}^3/_2\,(\text{total } H_2 \text{ used in } H_2O) \quad (1)$$

where g is the factor used to convert pressure readings at −180° to corresponding values at 25°. This factor was determined empirically with mixtures of hydrogen and oxygen. It varied somewhat for different parts of the manometer, since different amounts of the reacting gases were exposed to room temperature while the reaction vessel was immersed in liquid oxygen; over a thirty centimeter range the factor varied from 3.03 to 3.11. On account of this variation, equation (1) is more accurately expressed by

$$H_2 \text{ used in HCl} = (g p_{-180°} - g' p'_{-180°}) - {}^3/_2\,(H_2 \text{ used in } H_2O)$$

where g and g' are the factors corresponding respectively to $p_{-180°}$ and $p'_{-180°}$. To prevent fluctuation of g with the temperature of the freezing-out liquid, pure liquid oxygen was used instead of liquid air.

Great accuracy cannot be claimed for this experimental procedure, but the reproducibility of runs shows that the method is adequate for the data desired.

Results and Discussion

For each run two curves were drawn, one a plot of the number of cm. of H_2 used in HCl formation against time, and the other a similar plot for the H_2 used in H_2O formation. From these curves data were obtained for a graph showing the distribution of H_2 between HCl and H_2O as a function of the O_2/Cl_2 ratio. The points on this graph were obtained by calculating for each interval of illumination the fraction of the total hydrogen consumed which was used in H_2O formation, and plotting this fraction against the average O_2/Cl_2 ratio for the interval. Unfortunately the curves for H_2O formation showed slight irregularities at the beginning of each run, so the first one or two intervals of illumination had to be discarded.

The graph obtained for runs in which the initial pressure of H_2 was about 30 cm. and in which the temperature was about 25° is shown in Fig. 1. The data for a typical run are given in Table I.

In the runs illustrated in Fig. 1, initial oxygen pressures were varied from 20 to 99 cm., and initial chlorine pressures from 4 to 32 cm. Hydrogen pressures were kept between 27 and 33 cm. Some of the runs were made with the reaction vessel thermostated at 25°, but results were equally satisfactory when the reaction vessel was exposed to the air.

TABLE I

Initial pressures: O_2 = 98.3 cm., H_2 = 28.8 cm., Cl_2 = 12.0 cm.

	Time, min.	Manometer reading, cm. at 25°	at −180°,	$\Delta p_{25°}$	H_2 in H_2O	HCl
	0	139.2	44.7			
1	20	138.6	43.65	0.6	0.8	1.8
2	50	137.6	42.55	1.6	1.3	4.0
3	80	136.3	41.75	2.9	1.95	5.1
4	110	135.0	41.1	4.2	2.7	5.9
5	150	133.5	40.3	5.7	3.5	6.8

Reading No. 1 discarded. For interval between readings 2 and 4: total H_2 used = 3.3; H_2 used in H_2O = 1.4; fraction of H_2 used in H_2O = 0.42. Average O_2/Cl_2 ratio = 97.3/6.9 = 14.1. For interval between readings 3 and 5: total H_2 used = 3.25; H_2 used in H_2O = 1.55; fraction of H_2 used in H_2O = 0.48. Average O_2/Cl_2 ratio = 95.6/5.9 = 16.2.

The curve in Fig. 1 shows clearly that as the ratio of O_2 to Cl_2 increases, the fraction of the available H_2 which combines with O_2 does not increase indefinitely, but approaches a limiting value asymptotically. The limit appears to be 2/3, but the data are not accurate enough to fix this value with certainty. In the experiments of Chapman and Watkins[1] mentioned above, average O_2/Cl_2 ratios as high as 250/1 were used, and in all of their runs the fraction (H_2 in H_2O/total H_2) remained under 2/3. It is a little difficult to compare directly the data of these investigators with the present work, since they were concerned only with the products obtained after twelve hours of illumination with sunlight. If simple averages over the twelve-hour periods are used for chlorine concentrations, and if initial oxygen pressures are used, the figures in Table II are obtained. Agreement with the data in Fig. 1 is fairly good, and the approach to a limit between 0.6 and 0.7 seems evident.

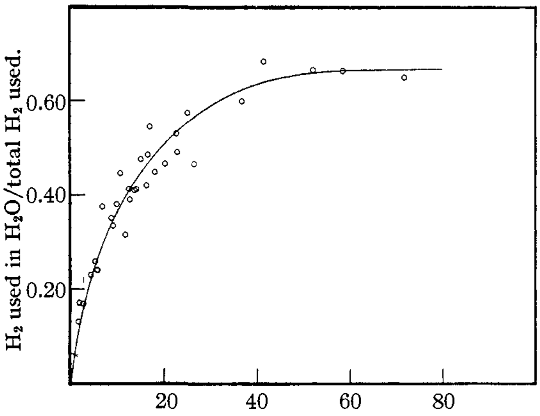

Fig. 1.

The existence of a limit can be accounted for if the Nernst chains are broken by a reaction of O_2

TABLE II

Initial $H_2 + O_2$, mml.	Average Cl_2, mml.	O_2/Cl_2	$\frac{H_2 \text{ used in } H_2O}{\text{total } H_2 \text{ used in 12 hr.}}$
Ratio $H_2/O_2 = 2/1$			
4.215	0.680	2.07	0.107
4.238	.608	2.32	.306
3.320	.0453	24.4	.359
Ratio $H_2/O_2 = {}^1/_2$			
8.330	.0626	88.9	.647
8.258	.0615	89.5	.593
6.189	.0400	103	.645
8.445	.0493	114	.583
8.802	.0323	181	.627
6.680	.0245	182	.633
6.073	.0157	258	.610

with H atoms, but not if they are broken by a reaction between O_2 and Cl atoms. For, if the chain-terminating step involves H atoms, then the rate of formation of water depends on the number of these atoms produced; but an H atom cannot be formed without the simultaneous production of an HCl molecule, no matter how small the Cl_2 concentration; and accordingly the ratio of H_2O formed to HCl formed will remain constant once the O_2 concentration is high enough to prevent the second reaction of the Nernst chain from taking place. On the other hand, if the chains are ended by a reaction involving Cl atoms, the fraction of H_2 used in water formation will show no dependence on the O_2/Cl_2 ratio, but will increase indefinitely as the O_2 concentration is increased. The point can be made clearer by a detailed consideration of the alternative mechanisms. The reactions initiating and propagating Nernst chains are

$$h\nu + Cl_2 = 2Cl \qquad (1)$$
$$Cl + H_2 = HCl + H \qquad (2)$$
$$H + Cl_2 = HCl + Cl \qquad (3)$$

These are followed by either

$$Cl + O_2 = ClO_2 \qquad (6)$$
$$\text{or } H + O_2 = HO_2 \qquad (9)$$

In addition to these five reactions, Norrish and Ritchie's[2] complete mechanism includes three others which will be discussed below

$$H + HCl = H_2 + Cl \qquad (4)$$
$$H + H_2 + O_2 = H_2O + OH \qquad (7)$$
$$H + HCl + O_2 = H_2O + ClO \qquad (8)$$

For convenience we have used Norrish and Ritchie's numbering of the steps. Bodenstein and Schenck[3] assume that reactions 6 and 9 require ternary collisions to stabilize the products. Norrish and Ritchie, in agreement with Bates and Lavin,[5] pronounce 9 a true bimolecular process and find it impossible from their data to pass judgment on 6. For simplicity we shall assume both reactions to be bimolecular; the argument is changed only slightly if they are considered to be trimolecular. The mechanism of H_2O formation from ClO_2 or HO_2 is a matter of speculation, but for present purposes the details are irrelevant. It is only necessary to assume that the rate of water formation is determined by the concentration of one or the other of these intermediates.

If all other possible reactions are neglected for the moment, the rate laws for HCl and H_2O may be derived very simply for the two skeleton mechanisms composed of reactions 1, 2, 3, 6 and 1, 2, 3, 9, respectively. If 6 is the chain-ending step

$$dHCl/dt = 2K_1K_2Cl_2 \cdot H_2/K_4O_2$$
$$dH_2O/dt = K_1Cl_2$$

Hence

$$\frac{dHCl}{dH_2O} = 2\frac{K_2}{K_4}\frac{H_2}{O_2}$$

and

$$\frac{H_2 \text{ used in } H_2O \text{ formation}}{\text{total } H_2 \text{ used}} = \frac{1}{1 + \frac{K_2}{K_4} \cdot \frac{H_2}{O_2}} \qquad (2)$$

The untenability of this reaction mechanism is indicated first of all by the expression for dHCl/d*t*, which bears no resemblance to any rate law which has been proposed. The formula for dH_2O/dt is probably nearly correct, although it needs correction by a small variable factor; Cremer[6] found that the rate of water formation is proportional to Cl_2, Bodenstein and Schenk find that the quantum yield of water formation is approximately constant, and the curves for dH_2O/dt in the present work show an approximate dependence on Cl_2.

According to equation (2), the fraction of H_2 which combines with O_2 should increase with the ratio O_2/H_2 and should approach a limit 1. The impossibility of such a relation is illustrated by Table III, which contains points selected from a number of different runs. The figures in the last five rows of Table III are taken from runs in which the initial pressure of H_2 was varied, and which are therefore not shown in Fig. 1. It can easily be shown that any conceivable reaction which might be added to reactions 1, 2, 3 and 6 would not remedy the disagreement between equation (2) and the data in Table III.

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[5] Bates and Lavin, THIS JOURNAL, **55**, 81 (1933).

[6] Cremer, *Z. physik. Chem.*, **128**, 285 (1927).

TABLE III

	Fraction of H_2 used in H_2O	O_2	H_2	Cl_2	O_2/H_2	O_2/Cl_2
			(Average values)			
1	0.18	18.7	6.8	10.4	2.7	1.8
2	.67	93.3	23.1	1.5	4.0	62.2
3	.62	91.5	22.3	2.5	4.1	36.6
4	.47	94.0	21.3	4.7	4.4	20.0
5	.24	76.7	17.4	13.7	4.4	5.6
6	.38	90.2	18.8	9.2	4.8	9.8
7	.21	49.8	10.3	11.7	4.8	4.3
8	.41	48.5	9.9	4.8	4.9	12.4
9	.27	49.3	7.9	8.5	6.2	5.8
10	.29	48.8	3.3	6.5	14.8	7.5
11	.56	90.7	3.3	2.6	27.5	34.9
12	.28	92.6	2.6	6.4	35.6	14.5
13	.41	95.1	1.2	3.3	79.2	28.8
14	.75	70.5	67.2	1.5	1.05	47.0
15	.51	43.9	76.2	3.4	0.58	12.9

While there is no way to reconcile reaction 6 as a chain-ending step with the curve in Fig. 1, formulas developed from reactions 1, 2, 3 and 9 are in very satisfactory agreement with the curve. This mechanism gives

$$\frac{dHCl}{dt} = K_1Cl_2 + 2\frac{K_1K_3Cl_2^2}{K_9O_2} \qquad (3)$$

$$\frac{dH_2O}{dt} = K_1Cl_2$$

Hence

$$\frac{dHCl}{dH_2O} = 1 + 2\frac{K_3}{K_9}\frac{Cl_2}{O_2} \qquad (4)$$

and

$$\frac{H_2 \text{ used in } H_2O}{\text{total } H_2} = \frac{2}{3 + \dfrac{K_3}{K_9}\dfrac{Cl_2}{O_2}} \qquad (5)$$

The rate law (3) is of course not the complete expression for dHCl/d*t*, but its general form agrees with the formulas for this rate in all recent work. It is identical with the expression which Bodenstein and Dux[7] long ago found suitable for a limited range of concentrations; the formula due originally to Thon which Bodenstein and Schenk use will reduce to (3) at small concentrations of Cl_2; and the formula derived by Norrish and Ritchie will reduce to (3) if the small first term in the denominator is omitted and if the trimolecular reactions 7 and 8 are neglected.

Equations (4) and (5) obviously have the right form: as Cl_2/O_2 grows smaller, the fraction of H_2 used in H_2O increases toward the constant value 2/3. These formulas are influenced only slightly by the insertion of new reactions in the mechanism. A detailed proof seems unnecessary, but three of the possible additional reactions are worth mentioning.

Norrish and Ritchie's step 4

$$H + HCl = H_2 + Cl$$

produces no effect whatever on any of the formulas (3–5). This reaction can influence the rate law only if some reaction besides 2 can remove Cl atoms.

The trimolecular reaction numbered 7 in Norrish and Ritchie's scheme

$$H + O_2 + H_2 = H_2O + OH$$

gives for equation (4)

$$\frac{dHCl}{dH_2O} = 1 + 2\frac{Cl_2}{O_2}\frac{K_3}{K_9 + K_7H_2}$$

and for equation (5)

$$\frac{H_2 \text{ used in } H_2O}{\text{total } H_2 \text{ used}} = \frac{2}{3 + \dfrac{2K_3Cl_2}{K_9O_2 + K_7H_2}} \qquad (6)$$

Thus, as O_2/Cl_2 increases, the fraction (H_2 in H_2O)/(total H_2) should still approach the limit 2/3, but the approach to this limit should be more rapid the higher the concentration of H_2. In other words, points for runs with low initial hydrogen concentrations should lie below the curve in Fig. 1 and points for runs with high H_2 concentrations should lie above, but at high values of O_2/Cl_2 all the points should lie close to the curve. Figure 2 is a plot of the runs made to test the effect of variation of H_2; the circles represent runs in which the initial concentration of H_2 was varied from 5 cm. to 10 cm., and the crosses illustrate runs in which the initial H_2 concentration was varied from 67 cm. to 83 cm. The curve is redrawn from Fig. 1. Points for low H_2 concentrations were difficult to obtain, since the H_2 is nearly used up before the irregularities in the H_2O

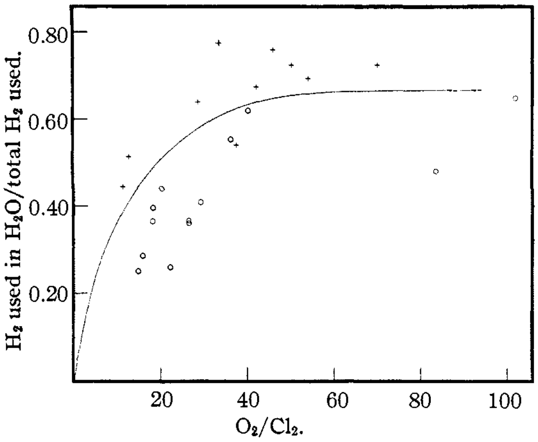

Fig. 2.—Circles refer to runs with initial H_2 pressures from 5 to 10 cm. Crosses refer to runs with initial H_2 pressures from 67 to 83 cm.

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[7] Bodenstein and Dux, *Z. physik. Chem.*, **85**, 297 (1913).

curves have disappeared; hence these points are widely scattered. Figure 2 corresponds to the requirements of equation 12 in a general way, but the limit for runs with high H_2 concentrations appears to be somewhat higher than that indicated in Fig. 1.

The inclusion of Norrish and Ritchie's reaction 8

$$H + HCl + O_2 = H_2O + ClO$$

with reactions 1, 2, 3 and 9 leads to

$$\frac{dHCl}{dH_2O} = \frac{1}{O_2} \cdot \frac{2K_3Cl_2 + K_7O_2}{K_9 + K_8HCl}$$

for equation (4) and

$$\frac{H_2 \text{ used in } H_2O}{\text{total } H_2 \text{ used}} = \frac{2}{2 + 2\dfrac{Cl_2}{O_2}\dfrac{K_3}{K_9 + K_8HCl} + \dfrac{K_1}{K_9 + K_8HCl}} \qquad (7)$$

for equation (5). The limit which (H_2 in H_2O)/(total H_2) approaches as O_2/Cl_2 increases is no longer constant, but is given by

$$(2K_9 + 2K_8HCl)/(3K_9 + 2K_8HCl)$$

an expression which varies between 2/3 for low concentrations of HCl and 1 for high concentrations. That is, very high concentrations of HCl would stop the formation of more HCl completely, and allow H_2 to be used exclusively in the formation of H_2O. Points obtained for runs in which HCl was added are shown by circles in Fig. 3; they lie well above the points in Fig. 1, as equation 13 requires. The crosses in Fig. 3 represent runs with no initial HCl, but in which high concentrations of HCl were built up by several hours of illumination. Another consequence of equation (7) is that the fraction (H_2 in H_2O)/(total H_2) should increase markedly in the course of a single run, since the HCl concentration builds up rapidly. To test this deduction, lines are drawn in Fig. 3 connecting the points belonging to each run for all the runs illustrated in Fig. 1. All but three of these lines are steeper than the part of the curve corresponding to the same abscissas. Similar connecting lines can be drawn for the nine runs illustrated in Fig. 2, and for the ten in Fig. 4; out of all these only one is not steeper than the curve.

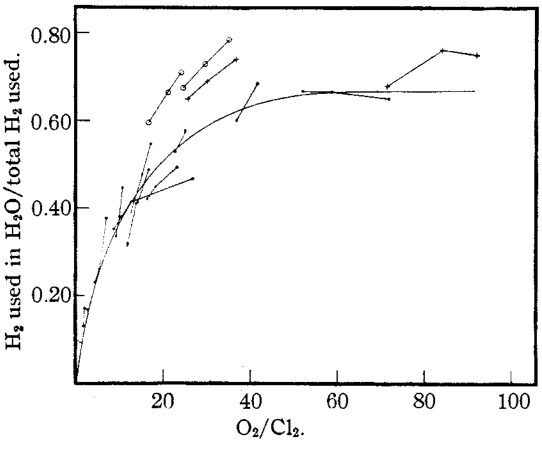

Fig. 3.—Dots represent points taken from Fig. 1. Circles refer to runs with 33 cm. of HCl present initially. Crosses refer to runs in which high concentrations of HCl were built up by several hours of illumination.

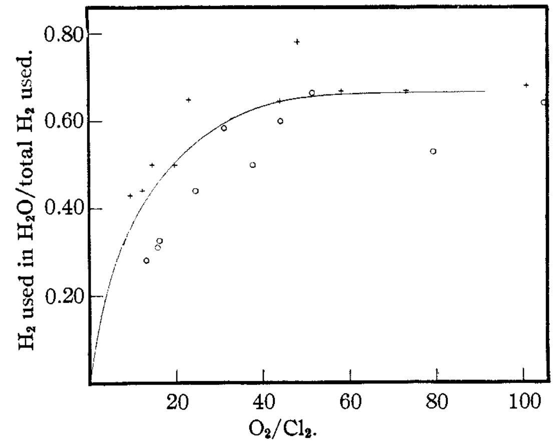

Fig. 4.—Circles refer to runs at 85°. Crosses refer to runs at 0°.

The general agreement of the data with formulas (6) and (7) furnishes a rather striking bit of evidence for the correctness of Norrish and Ritchie's reactions 7 and 8. If both these steps are included in the reaction mechanism, equation (5) becomes

$$\frac{H_2 \text{ in } H_2O}{\text{total } H_2} = \frac{2}{2 + \dfrac{Cl_2}{O_2}\dfrac{2K_3}{K_9 + K_7H_2 + K_8HCl} + \dfrac{K_9 + K_7H_2}{K_9 + K_7H_2 + K_8HCl}}$$

Whether the numerical value of the limit indicated by this formula is correct and whether the third term in the denominator is necessary cannot be decided from the data in Figs. 2 and 3. These graphs require simply an expression of the form

$$\frac{H_2 \text{ in } H_2O}{\text{total } H_2} = \frac{1}{K + \dfrac{Cl_2}{O_2} \cdot \dfrac{1}{K' + K''H_2 + K'''HCl}}$$

in which K must lie between 1 and 3/2, and may show a slight variation with H_2 or HCl.

The effect of temperature remains to be considered. For this purpose runs made at 0° and runs made at 85° are plotted on Fig. 4, together with the curve from Fig. 1 for runs at 25°. An increase in temperature evidently causes a slight increase in the proportion of H_2 which combines with Cl_2.

When the O_2/Cl_2 ratio is 20, a rough estimate gives a value 0.57 for the fraction (H_2 in H_2O)/(total H_2) in the 0° runs and a value 0.40 for the fraction in the 85° runs. Corresponding to these figures are values for the ratio $dH_2O/dHCl$, 0.65 at 0° and 0.33 at 85°. The activation energy calculated for such a change of rate with temperature would be about 1600 calories, which is therefore the difference in activation energies between the reactions leading to HCl formation and those leading to H_2O formation. Since the relative rates at which HCl and H_2O are formed depends on the distribution of H atoms between reactions 3 and 9

$$H + Cl_2 = HCl + Cl \qquad (3)$$
$$H + O_2 = HO_2 \qquad (9)$$

the value 1600 may be considered as the difference in activation energies for these two reactions. Both 3 and 9 are highly exothermic and presumably require very little activation, so 1600 calories is a reasonable figure for the difference in activation energies. Bodenstein and Schenk calculate a value 1900 calories for this quantity from some work of Hertel[8] on the temperature coefficient of the HCl reaction.

Summary

The rates of formation of HCl and H_2O in illuminated mixtures of H_2, Cl_2 and O_2 have been measured for high concentrations of O_2. As the ratio O_2/Cl_2 increases, the ratio (H_2O formed)/(HCl formed) approaches a limit between 1 and 2.

The rate at which the limit is approached increases slightly with increasing concentrations of H_2 and HCl. It is possible that the value of the limit also may be somewhat higher when high concentrations of H_2 or HCl are present.

The rate of approach to the limit shows a slight dependence on the temperature, indicating that the activation energy for the reactions leading to HCl formation is slightly greater than for those leading to H_2O formation.

The existence of this limit proves that the Nernst chains must be ended by a reaction $H + O_2 = H_2O$ rather than by $Cl + O_2 = ClO_2$. The occurrence of this latter reaction to a slight extent is not prohibited, but it must be of secondary importance compared to the former.

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[8] Hertel, *Z. physik. Chem.*, **B15**, 325 (1932).

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A Procedure for the Preparation of Uniform Nephelometric Suspensions

BY ARTHUR F. SCOTT AND FRANK H. HURLEY

It is a well-known fact that the optical properties of silver chloride suspensions are influenced by the conditions attending their preparation. Although no systematic study of these conditions has been made, there is sufficient evidence[1] to indicate that the rate of addition of the precipitant is a factor of primary importance. It would appear, therefore, that the reproducibility of nephelometric suspensions would be increased considerably if the precipitant could be added in exactly the same manner in every preparation, a condition which cannot be fully satisfied by the usual procedure of adding the precipitant dropwise ("stirring" method) or of pouring the sample of solution into the precipitant ("pouring" method). The present paper describes a device whereby the desired condition of uniform addition of the precipitant may be achieved readily.

A convenient form of this precipitating device, designed to meet the special requirements of the analysis of a pure chloride compound by the Richards method, is shown in Fig. 1.[2] In analyses of this sort, suspensions of silver chloride are prepared by the addition of a 2-ml. portion of the precipitant, either silver nitrate ("excess Ag") or sodium chloride ("excess Cl") solutions, to a 20-ml. sample of the supernatant analytical solution, which is saturated with silver chloride. To fill the vessel, shown upright in Fig. 1, it is

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[1] Kleinmann, *Biochem. Z.*, **99**, 149 (1919); Scott and Moilliet, THIS JOURNAL, **54**, 208 (1932); Kober, *Ind. Eng. Chem.*, **10**, 558 (1918).

[2] The design of this vessel is adapted from one used by Jolibois [*Compt. rend.*, **169**, I, 1096 (1919)] to produce rapid and uniform mixing of two solutions. See also Sheppard and Lambert, "Colloid Symposium Monograph," **6**, 265 (1928).