ume at the equivalence point was made 500 cc. instead of 200 cc. as was the case with the titrations given in Table I (a) and (b). In spite of this dilution a definite maximum $\Delta E/\Delta$ cc. point could be detected and the agreement between the observed and the theoretical equivalence points was about 1.5 parts per 100.

In order to determine the commercial applicability of the above potentiometric method the arsenate content of a commercial sample of calcium arsenate was determined volumetrically and potentiometrically in the following manner. The volumetric determination was made by reduction of the arsenate to arsenite followed by subsequent oxidation of the arsenite by standard iodine solution. The potentiometric method consisted of an adaptation of the method used by Bedford, Lamb and Spicer,[4] in which the titration was made after the addition of buffer and the required amount of alcohol.

Due to the relatively high ionic strength of the solution treated as above, the maximum value of $\Delta E/\Delta$ cc. was found to be about 25 millivolts per cc. Nevertheless, the maximum was easily detectable. Two volumetric determinations gave as the As_2O_5 content of the sample 40.38 and 40.11%, respectively, while two potentiometric determinations showed 39.93 and 39.66% As_2O_5.

Summary

1. Using sodium acetate as a buffer it is possible to determine potentiometrically the arsenate content of acid arsenates.

2. The optimum conditions for the determination consist in using ten times the theoretical amount of acetate necessary to react with the acid formed in the reaction, in a solvent consisting of 50% alcohol by volume.

3. The potentiometric method of determination can be used for the determination of the arsenate content of a commercial sample of calcium arsenate.

WORCESTER, MASS. RECEIVED OCTOBER 21, 1933

[4] Ref. 2, p. 588.

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

A Correlation of the Photosyntheses of Phosgene and Hydrogen Chloride

BY G. K. ROLLEFSON

The two photochemical reactions involving chlorine which have been most extensively studied are those with hydrogen and carbon monoxide to give hydrogen chloride and phosgene, respectively. In each of these systems it has been shown that the reaction proceeds by a chain mechanism consisting of a pair of reactions, one using up chlorine atoms and the other forming them. The number of chains started is determined by the number of light quanta absorbed and the chain length is determined by the relative rates of the reactions which result—directly or indirectly—in the elimination of chlorine atoms and the reaction which continues the chain. A study of the kinetics of the two systems has shown that the chain terminating reactions are different. That for the phosgene reaction involves COCl and Cl[1] whereas the hydrogen chloride reaction requires a reaction of Cl atoms at the wall or with some impurity.[2] As the concentrations of chlorine atoms and the intermediate COCl are not known it is not possible to estimate the magnitude of the rate constants for the chain terminating processes nor for the chain continuing reactions by such studies. If, however, we take mixtures of carbon monoxide, hydrogen and chlorine and illuminate with light absorbed by the chlorine we may consider that the reactions resulting in the recombination of chlorine atoms (whatever they may be) are the same for both possible chains. The reactions in such a system may be formulated as follows

(1) $Cl_2 + h\nu = Cl + Cl^*$
(2) $Cl + H_2 = HCl + H$
(2a) $Cl + Cl_2 + CO = COCl + Cl_2$
(3) $H + Cl_2 = HCl + Cl$
(3a) $COCl + Cl_2 = COCl_2 + Cl$

with chain terminating processes such as

$$(4)\quad \begin{array}{l} COCl + Cl = CO + Cl_2 \\ Cl + Cl = Cl_2 \\ Cl + \text{wall} = {}^1/_2Cl_2 \end{array}$$

the relative amounts of HCl and $COCl_2$ formed, in such a mixture will be determined by the rates

---

[1] (a) Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, **B3**, 459 (1929); (b) Lenher and Rollefson, THIS JOURNAL, **52**, 500 (1930).

[2] Bodenstein and Unger, *Z. physik. Chem.*, **B11**, 253 (1931).

of (2) and (2a) two molecules of hydrogen chloride resulting each time the sequence (2) and (3) occurs and one of phosgene each time we have (2a) and (3a). The fraction of the chlorine molecules reacting which react with hydrogen according to this scheme is measured by $\Delta H_2/\Delta H_2 + \Delta CO$ and it may be shown that this follows the law

$$\text{(I)}\quad \frac{\Delta H_2}{\Delta H_2 + \Delta CO} = \frac{k_2(Cl)(H_2)}{k_2(Cl)(H_2) + k_{2a}(Cl)(CO)(Cl_2)} = \frac{1}{1 + \frac{k_{2a}}{k_2}\frac{(CO)(Cl_2)}{H_2}}$$

The steps (2a) and (3a) used in deriving this law are taken from the mechanism for phosgene formation given by Lenher and Rollefson;[1b] (2) and (3) are the usual Nernst chain steps. Now according to some calculations of Rollefson and Eyring[3] there is a marked tendency for Cl_3 to form from Cl and Cl_2 such that if equilibrium is attained the ratio of Cl_3 to Cl is fairly large at moderate pressures of chlorine. In order that Cl_3 be at its equilibrium concentration its rate of formation from Cl and Cl_2 and the rate of decomposition must be fast compared to any other reactions involving Cl or Cl_3. As we shall see later in our discussion, this is not improbable. Such being the case, we should replace Cl in (2) by Cl_3 and Cl + Cl_2 in (2a) by Cl_3 which would cause the law for the fraction of the chlorine forming HCl to assume the form

$$\text{(II)}\quad \frac{\Delta H_2}{\Delta H_2 + \Delta CO} = \frac{1}{1 + \frac{k_{2a}}{k_2}\frac{(CO)}{(H_2)}}$$

Some other possibilities should be considered. If the atomic chlorine reacts with hydrogen but (2a) involves Cl_3, whether it is at its equilibrium concentration or not, we would obtain an equation of the form of I. If we follow the suggestion of Bodenstein, Lenher and Wagner[1a] that (2a) be replaced by $CO + Cl \rightleftarrows COCl$ in which equilibrium is established followed by $COCl + Cl_2 = COCl_2 + Cl$, then we would also obtain I since the effect of these two successive reactions is kinetically identical with (2a). Still another possibility which might be suggested is that chlorine atoms react with hydrogen or carbon monoxide in simple bimolecular reactions. This scheme would give II but we may disregard it as being imcompatible with the known facts of the photosynthesis of phosgene.

In order to test a given set of data to determine which of these two laws is obeyed, it is most convenient to plot the reciprocal of the fraction of the chlorine reacting with hydrogen against the ratio $(CO)/(H_2)$ or $(CO)(Cl_2)/(H_2)$ as the case may be. The plot which represents the correct law will be a straight line with an intercept of one on the ordinate axis and a slope equal to k_{2a}/k_2. The data to be presented in this paper will show that the correct form of the law in this system is the one involving $(CO)/(H_2)$.

Experimental Procedure and Results

The data which are needed are determinations of the amounts of hydrogen chloride and phosgene formed on illuminating mixtures of carbon monoxide, chlorine and hydrogen of different compositions. From the equations

$$CO + Cl_2 = COCl_2$$
$$H_2 + Cl_2 = 2HCl$$

we see that any pressure change which may occur with the reaction mixture at 0° is due to the formation of phosgene. If we lower the temperature to −180° everything will freeze out except the carbon monoxide and hydrogen, thus making it possible to determine the change in the sum of these two gases and by combining these data with the pressure change at 0° we obtain the amounts of $COCl_2$ and HCl formed. In order to have the pressure readings as accurate as possible, they were taken at 0° and at the boiling point of oxygen, *i. e.*, −183°. The observed pressure change at −183° was corrected to 0° by an empirical "freeze-out" factor which was determined experimentally at the start of the run. The procedure may be illustrated by the following typical run. Pressures are expressed in cm. of sulfuric acid.

The sulfuric acid manometer was connected directly to the reaction vessel through about one meter of 1-mm. capillary tubing. Numerous tests with various reactions have shown that no disturbances are introduced by this arrangement.

Zero reading of the manometer 0.80

Initial pressures $Cl_2 = 29.90$. $H_2 = 9.55$, $CO = 51.30$

$$\text{Initial manometer readings}\begin{cases} 0° & 91.55 \\ -183° & 22.50 \end{cases}$$

Illuminated 25 sec. at 0° mean values $H_2 = 8.70$, $Cl_2 = 28.0$, $CO = 50.22$

$$\text{Manometer readings}\begin{cases} 0° & 89.40 & \Delta p = 2.15 \\ -183° & 21.10 & \Delta p' = 1.40 \end{cases}$$

$\Delta CO = \Delta p = 2.15$

$\Delta CO + \Delta H_2 = 2.80 \times \Delta p' = 3.92 \quad \Delta H_2 = 1.77$

$\Delta H_2 + \Delta CO/\Delta H_2 = 2.21 \quad (CO)/(H_2) = 5.75$

---

[3] Rollefson and Eyring, THIS JOURNAL, **54**, 170 (1932).

Illuminated 25 sec. at 0° mean values $H_2 = 7.20$. $Cl_2 = 24.37$, $CO = 48.0$

$$\text{Manometer readings} \begin{cases} 0° & 87.33 & \Delta p = 2.07 \\ -183° & 19.88 & \Delta p' = 1.22 \end{cases}$$

$\Delta CO = 2.07$

$\Delta H_2 + \Delta CO = 3.42 \quad \Delta H_2 = 1.35$

$(\Delta H_2 + \Delta CO)/\Delta H_2 = 2.54 \quad (CO)/(H_2) = 6.66$

A summary of the data obtained at 0° and also at 32° is contained in Tables I and II, respectively. The values listed for $(CO)/(H_2)$ and $(CO)(Cl_2)/(H_2)$ are calculated, using the average pressures of the reacting substances. The amount of reaction was always so small that these ratios did not differ appreciably from the mean value of the ratio during the period of illumination. In carrying out the experiments at 32° the reaction mixture was at that temperature only for the period of illumination, all the pressure readings being taken at 0° and −183°. The temperature, 32°, was taken merely because it was easy to maintain with the heating arrangement used and at the same time gave results markedly different from those at 0°. The values of $(CO)(Cl_2)/(H_2)$ are not listed at this temperature as it was obvious from the work at 0° that the CO/H_2 ratios were the ones that were needed. The results at 0° are represented graphically in Fig. 1, in which the ordinates are the reciprocals of the fraction of the chlorine reacting with hydrogen and the abscissas are the carbon monoxide–hydrogen ratios. While there is some scattering of the points it is obvious that the linear relationship is fulfilled. The scattering is to be expected as the errors in reading the small differences on the manometer are quite large. If we make a plot using the $(CO)(Cl_2)/(H_2)$ ratios we find that no single straight line can be drawn, hence we must conclude that the division of the chlorine between the two reactions is a function solely of the carbon monoxide and hydrogen pressures.

TABLE I

Temperature 0°C.

Composition H_2	Cl_2	CO	$\frac{(CO)}{(H_2)}$	$\frac{(CO)(Cl_2)}{(H_2)}$	$\frac{\Delta H_2 + \Delta CO}{\Delta H_2}$
26.9	21.1	22.7	0.84	17.8	1.16
10.8	63.0	10.7	0.99	62.3	1.20
8.9	66.0	9.5	1.06	69.8	1.26
21.9	28.9	23.8	1.08	31.3	1.24
19.8	26.2	23.0	1.17	30.6	1.24
7.8	59.2	9.9	1.27	75.3	1.35
6.4	62.4	8.5	1.34	83.5	1.44
10.2	23.4	17.9	1.75	41.0	1.34
8.9	52.6	17.4	1.94	102	1.55
7.6	19.7	16.8	2.21	43.5	1.43
13.5	39.0	33.4	2.46	96.2	1.61
7.7	64.1	20.0	2.60	167	1.70
5.8	17.2	16.1	2.78	47.7	1.45
5.3	46.5	14.9	2.82	131	1.93
10.8	34.3	31.3	2.90	99.5	1.81
6.0	60.8	18.6	3.10	188	1.96
10.3	35.2	35.8	3.48	122	1.85
4.8	58.2	17.3	3.60	212	2.14
3.4	43.3	12.7	3.74	162	2.32
8.5	31.7	34.1	4.01	127	2.04
[x]5.8	26.0	24.9	4.30	112	2.26
6.9	28.2	32.2	4.68	132	2.17
8.7	28.0	50.1	5.75	162	2.21
8.5	52.4	52.8	6.20	325	2.46
7.8	50.5	51.5	6.60	334	3.26
7.2	24.4	48.0	6.66	162	2.54
6.0	22.7	46.1	7.68	174	2.40
6.5	50.9	51.3	7.90	402	3.05
5.9	49.2	50.1	8.50	418	2.83

[x] 23 cm. pressure of $COCl_2$ also present.

TABLE II

Temperature, 32°

Composition H_2	Cl_2	CO	$\frac{(CO)}{(H_2)}$	$\frac{\Delta H_2 + \Delta CO}{\Delta H_2}$
6.0	33.8	28.3	4.8	1.31
7.4	23.5	55.7	7.6	1.45
4.4	28.1	48.2	11.0	1.64
5.0	25.0	56.4	11.3	1.64
4.5	28.0	54.6	12.1	1.90
4.0	23.1	55.6	13.9	1.89
3.4	26.4	47.5	14.0	1.79
3.8	27.4	56.5	14.9	1.78
2.9	27.2	52.5	18.1	2.36
2.52		48.3	19.0	1.95
2.4	25.3	51.4	21.4	2.70
1.51		47.1	31.2	2.56

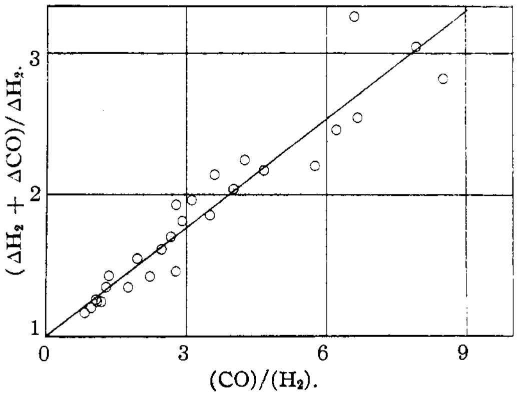

Fig. 1.

The effect of temperature on the system is quite marked. The slope of the line obtained from the data at 0° is 0.256 and at 32° is 0.060 and, from what has been stated in the introductory part of this paper, these are the values of k_{2a}/k_2 at the two temperatures. Considering that in general a rate constant is given by an equation of the form $k = se - Q/RT$, we may write

$$\frac{k_{2a}}{k_2} = \frac{s_{2a}}{s_2}e^{-(Q_{2a} - Q_2)/RT}$$

$$\ln\frac{k_{2a}}{k_2} = \ln\frac{s_{2a}}{s_2} + \frac{Q_2 - Q_{2a}}{RT}$$

If we have k_{2a}/k_2 for two different temperatures we may solve for s_{2a}/s_2 and $Q_2 - Q_{2a}$. Substituting the values given above, we find for the system under consideration

$$s_{2a}/s_2 = 3.67 \times 10^{-7} \quad Q_2 - Q_{2a} = 7.25\ k\ \text{cal.}$$

The uncertainty in $Q_2 - Q_{2a}$ is not greater than one kilocalorie with a corresponding uncertainty in the value of s_{2a}/s_2.

Discussion

One conclusion which may be drawn from the data presented in this paper is that the equilibrium $CO + Cl \rightleftarrows COCl$ postulated by Bodenstein, Lenher and Wagner cannot be an essential step in the phosgene mechanism. The only effect the hydrogen could have on such an equilibrium would be that it would reduce the chlorine atom concentration and thus reduce the COCl concentration but this new concentration would be an equilibrium value. The division of the chlorine between the two possible reactions would have to follow a law of the form of I whether we consider the phosgene to be formed in an indefinite way according to $CO + Cl + Cl_2 = COCl_2 + Cl$ as originally suggested by Bodenstein, Lenher and Wagner or whether we use the later view given by Schumacher and Stieger[4] that the reaction is $COCl + Cl_2 = COCl_2 + Cl$. The fact that the observed law is definitely of the form of II must be considered as eliminating the possibility of $CO + Cl \rightleftarrows COCl$ being at equilibrium.

The experimental data which have been presented indicate that we must consider that the molecule, Cl_3, is the reactive form of chlorine involved in both the phosgene and hydrogen chloride syntheses at moderate pressures.[5] This is directly contrary to the conclusions of Kimball and Eyring,[6] who calculated activation energies for Cl and Cl_3 with H_2 and found that for Cl to be about 5 kcal. lower than that for Cl_3. There are some considerations, however, which are unfavorable to their views. In the first place the calculated activation energies are much too high; the experimental results of Rodebush and Klingelhoefer[7] and von Hartel and Polanyi[8] at low pressures where Cl_3 may be neglected indicate a value of approximately 6 kcal. for the reaction between Cl and H_2 whereas the calculated value is about 16 kcal. If we reduce the calculated activation energy for the reaction involving Cl_3 a corresponding percentage we obtain a value a little less than 8 kcal. so that the fraction of the total number of collisions having the necessary activation energy differs by a factor of only 20 in the two cases instead of nearly 4000. In addition to this we must consider that if Cl_3 is stable with respect to Cl_2 and Cl then the preponderance of Cl_3 over Cl would offset any small factor due to a difference in the heats of activation. Furthermore, the factor s in the equation $k = se^{-Q/RT}$ may be such for these two molecules that Cl_3 is the more reactive. Taking all these possibilities into consideration, we see that the theoretical objections to Cl_3 do not rest on a very solid foundation.

If Cl_3 is taken as the active substance then it is of interest to decide whether or not it is present at equilibrium concentration with respect to Cl_2 and Cl. For equilibrium to be maintained it is necessary that the rates of formation and decomposition of Cl_3 shall be fast compared to the reactions involving Cl_3. No experimental data are available concerning the rates involved in this equilibrium so we must seek a clue in the calculations of Rollefson and Eyring.[3] According to their calculations the heat of activation for the formation of Cl_3 is 4.5 kcal. and for the decomposition 8.6 kcal. If we assume that every collision with sufficient energy is effective for formation, the specific rate constant, in moles per liter per sec., becomes $10^{11}e^{-4500/2\times 273} = 3.3 \times 10^7$. For the decomposition let us assume that we may calculate the equilibrium constant which is the ratio of the specific rate constants. The value obtained is 95,[9] which gives for the specific decomposition rate 3.5×10^5. From the data presented in the experimental part of this paper we see that even if we assume that CO reacts with Cl_3 without activation, the maximum value that the rate constant can have is[10] 3.67×10^4 or approximately

---

[4] Schumacher and Stieger, *Z. physik. Chem.*, **B13**, 157 (1931).

[5] As far as the data which have been presented are concerned $Cl + Cl_2$ is just as satisfactory as Cl_3, the sole question being whether the reactions are bimolecular involving Cl_3 or trimolecular involving $Cl + Cl_2$. The fact that Cl_2 cannot be replaced by other gases in this step in the phosgene reaction is strongly in favor of the Cl_3 formulation and the remainder of this paper is devoted to showing that this is not inconsistent with other data.

[6] Kimball and Eyring, THIS JOURNAL, **54**, 3876 (1932).

[7] Rodebush and Klingelhoefer, *ibid.*, **55**, 130 (1933).

[8] Von Hartel and Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

[9] Rollefson and Eyring, THIS JOURNAL, **54**, 173 (1932).

[10] This figure is derived by assuming that k for the reaction of Cl_3 with H_2 is given by $10^{11}e^{-Q/RT}$, *i. e.*, every collision involving the energy Q is effective; then according to the data given the k for the reaction with CO is $10^{11} \times 3.67 \times 10^{-7}e^{-Q/RT}$. Assuming $Q = 0$ for the latter, we obtain the value given.

one-tenth the decomposition rate. A similar value may be calculated for the reaction between H_2 and Cl_3. From the nature of the assumptions we have used we must consider that the latter values are maximum ones and should be diminished by a factor depending on the magnitude of the heat of activation of the reaction between carbon monoxide and Cl_3. It is quite possible, therefore, that this active intermediate, Cl_3, could be present at its equilibrium concentration. Under such circumstances a change of temperature should change the concentration of this molecule and the observed temperature coefficients should involve the heat of dissociation of Cl_3. The temperature coefficient for the phosgene formation involves so many terms due to the various steps in the mechanism that it is difficult to draw any conclusions from that source. For the hydrogen chloride formation, however, the situation is much more simple. In this case at moderate pressures the temperature coefficient will depend upon (a) the heat of dissociation of Cl_3, (b) the heat of activation of the reaction between Cl_3 and H_2, (c) the heat of activation of the chain terminating process. At low pressures where atomic chlorine predominates the heat of activation depends on the difference between the heats of activation for the reaction between Cl and H_2 and the chain terminating reaction. The net heat of activation in the first instance may be obtained from the work using light of wave length 3600 Å. as there is no need to correct for the change in light absorption with temperature at that wave length. Padoa and Butironi[11] give a temperature coefficient which corresponds to $Q = 2.8$ kcal. Some unpublished work in this Laboratory[12] gives 2.5 kcal., so we may consider 2.6 ± 0.2 kcal. as a reasonable value. No measurements of the temperature coefficient of the photochemical reaction at low pressures are available but we may use the data of Rodebush and Klingelhoefer. Their data were obtained by using chlorine atoms from an electric discharge tube but there is no essential difference between such chlorine atoms and those obtained by the action of light on chlorine molecules. They found a temperature coefficient corresponding to an activation energy of 6.1 ± 1.0 kcal. The difference between this value and the one obtained at higher pressures must be attributed to the heat of dissociation of Cl_3 and the difference between the heats of activation for the reactions of Cl and Cl_3 with hydrogen. From the data presented earlier in this paper we may conclude that the heat of activation for Cl_3 reacting with hydrogen is not less than 7.25 ± 1.0 kcal. or slightly higher than the value for atomic chlorine. The heat of dissociation of Cl_3 on this basis would have to be at least 4.4 kcal. for the net observed heat of activation to be 2.8 kcal. An upper limit for the heat of dissociation of Cl_3 may be estimated if we assume that in the experiments of Rodebush and Klingelhoefer the ratio of Cl to Cl_3 was at least one. Such an assumption leads to a value of 6.0 kcal. so we may say that a reasonable value in the light of existing data is 5.0 ± 1.0 kcal.

Summary

It has been shown that the active form of chlorine involved in the chain processes of the phosgene and hydrogen chloride photosyntheses is the same. From a consideration of the mechanism for the formation of phosgene and some theoretical calculations, the formula, Cl_3, is assigned to this intermediate. It is shown that a molecule of this formula is consistent with the observations on the temperature coefficient for the hydrogen chloride formation and a value for the heat of dissociation into a chlorine atom and a chlorine molecule is given.

BERKELEY, CALIF. RECEIVED OCTOBER 23, 1933

---

(11) Padoa and Butironi, *Atti. accad. Lincei*, **25**, 11, 215 (1916).

(12) J. C. Potts, M.S. Thesis, University of California, 1932.