

hexane or the alcohol-cyclohexane mixture contains water.

A study of the polarity of the liquids used may throw some light on their solubility behavior. It is generally accepted that polar liquids are soluble in polar liquids, and non-polar liquids are miscible in each other, while substances distinctly non-polar are immiscible in polar liquids. Thus the highly polar nature of water and the lesser polarity of methyl alcohol as compared with the extremely non-polar nature of cyclohexane may account for the miscibility of methyl alcohol and water, the immiscibility of water and cyclohexane, and the partial miscibility of methyl alcohol and cyclohexane.

In considering the ternary systems consisting of water, an alcohol and a hydrocarbon, the liquids may be listed in the order of their dielectric constants: water 81, methyl alcohol 33.1, ethyl alcohol 26, benzene 2.28 and cyclohexane 2.05.⁹

By distribution experiments the greater amount of the alcohol is found in the water-rich layer in each case. The alcohol thus functions chiefly in tending to bring the polarity of the water nearer to that of the hydrocarbon. Since methyl alcohol is more polar than ethyl alcohol, it might be expected that there would be a greater area be-

(9) "International Critical Tables," The McGraw-Hill Book Co., Inc., New York, Vol. VI, 1928, pp. 83-91.

neath the binodal curve in the case of methyl alcohol-cyclohexane-water than with ethyl alcohol-cyclohexane-water.¹ This is substantiated by experiment. Similarly, the binodal curve for methyl alcohol-benzene-water¹⁰ is higher than that for ethyl alcohol-benzene-water.¹

Since benzene is slightly more polar than cyclohexane, the binodal curves of the two systems containing cyclohexane are above those containing benzene.

If these binodal curves are re-drawn, the concentration being expressed in mole per cent. using the usual molecular weights rather than in weight per cent., these differences are even more pronounced.

Summary

1. The equilibrium concentrations for the system methyl alcohol-cyclohexane-water at 25°, and tie-lines for this system have been determined.

2. The freezing point curve for solutions of methyl alcohol in cyclohexane has been determined.

3. It has been shown that a consideration of polarity gives a means of locating in a relative manner the binodal curves of some analogous ternary systems.

(10) Barbaudy, *Compt. rend.*, **182**, 1279 (1926).

LINCOLN, NEBR.

RECEIVED OCTOBER 13, 1933

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

The Thermal Reaction between Chlorine Trioxide and Ozone

BY G. K. ROLLEFSON AND A. C. BYRNS

Some time ago an investigation of the chlorine sensitized photochemical decomposition of ozone was started in this Laboratory. The preliminary experiments indicated that the system involved several parallel reactions so our attention has been concentrated on the isolation and study of these component reactions. The first indication that one of these could be isolated came from a study of the pressure change *vs.* time curves obtained when mixtures of chlorine and ozone were illuminated with blue light. These curves showed a marked decrease in the rate with time of illumination similar to that reported by Heidt, Kistiakowsky and Forbes.¹ At the same time a

(1) Heidt, Kistiakowsky and Forbes, *THIS JOURNAL*, **55**, 223 (1933).

comparison of the oxygen pressure as calculated from the pressure change with the value obtained by freezing out all the other gases with liquid air revealed that much more oxygen was being formed than corresponded to the observed pressure change. Obviously this indicated the presence of another reaction which was causing a pressure decrease. A typical run illustrating this behavior is given in Table I. An examination of the

TABLE I
Initial Cl₂, 61 cm.; initial O₃, 69 cm.

Time, min.	Δp	O ₂ from Δp	O ₂ from freeze-out	Difference
90	7.49	22.5	40.6	18.1
175	11.97	35.9	67.3	31.4
220	14.90	44.7	82.8	38.1

reaction vessel toward the end of the run revealed that an oily red liquid had separated. When the illumination was carried on with the reaction vessel at 0° instead of at 21°, the amount of liquid obtained was considerably greater.

The empirical formula of this compound was determined by decomposing it and analyzing the resulting gases for chlorine and oxygen. Chlorine-oxygen ratios of 1:3 corresponding to the formula ClO_3 were obtained, indicating that we were dealing with the oxide which has been reported in the literature under similar circumstances.² Allmand and Spinks³ have postulated the catalysis of the decomposition of ozone by this compound although they did not isolate the oxide. Furthermore Bodenstein, Padelt and Schumacher⁴ have assumed a reaction between ClO_3 and ozone in their mechanism for the chlorine catalysis of the thermal decomposition of ozone. Therefore we turned our attention to the study of the reaction of this oxide with ozone.

The oxide was prepared as needed by illuminating a mixture of ozone and chlorine in the reaction vessel. The gases were pumped off the oxide and it was frozen and liquefied several times while evacuating so as to remove the last traces of impurities. The final product was solid when the reaction vessel was surrounded by an ice-bath but melted within a few seconds after the bath was removed. This indicates a melting point slightly above 0° instead of -1° as reported by Bodenstein, Harteck and Padelt. We consider this as evidence that our oxide was quite pure.⁵

Chlorine was prepared by heating anhydrous cupric chloride in a small tube connected to the reaction vessel.

The ozone was prepared from electrolytic oxygen by a silent electric discharge and the ozone together with the excess oxygen was condensed in a liquid air trap. When sufficient ozone had been produced the trap was shut off from the ozonizer and the oxygen pumped off, keeping the ozone at liquid air temperatures. The ozone was distilled from this trap to the reaction vessel by immersing the latter in liquid air and allowing the trap to warm up. Any oxygen produced in this process, usually only a few millimeters, was pumped off, using a mercury vapor pump protected by a liquid air trap.

All of the oxygen used was prepared by the electrolysis of a solution of potassium hydroxide, traces of hydrogen were removed with hot copper oxide and the gas dried by passing it over phosphorus pentoxide. The nitrogen was taken from a commercial tank, was passed through a

tower containing copper turnings and ammonium hydroxide to remove oxygen, and then dried with sulfuric acid and phosphorus pentoxide, which also removed any ammonia from the previous treatment.

The reaction vessel was made of Pyrex glass, cylindrical in form with a diameter of approximately 5 cm. and a length of 12 cm. This vessel was maintained at constant temperature by immersing it in a bath of ice and water for the work at 0° and in a thermostat which was hand regulated to $\pm 0.05^\circ$ for the work at 20°. Pressures were read with a manometer filled with concentrated sulfuric acid (d 1.84) and the results are recorded in such units.

The procedure followed was to prepare and purify a small amount of the oxide in the reaction vessel, cool with liquid air and distil some ozone. Then the liquid air was removed, the vessel immersed in the thermostat at the desired temperature, and the reaction followed by observing the change in pressure. The time zero for the reaction was taken as one minute after immersing the reaction vessel in the thermostat. This introduced a small error as some reaction occurred as the mixture was being warmed up to the temperature at which observations were made. The magnitude of this error may be seen from an examination of the data in Table II, which gives a comparison of the oxygen pressure as determined by freezing out the other gases with liquid air and measuring the residual pressure and the oxygen pressure calculated on the assumption that the net reaction causing a pressure change is $2\text{O}_3 = 3\text{O}_2$.

TABLE II

Temp., °C.	p_{O_2} exp.	p_{O_2} calcd.	Initial ozone press., cm.
20	72.7	70.1	86.0
20	136.3	132.1	79.0
20	60.1	57.7	110.0
0	6.9	6.5	51.3
0	17.4	15.3	110.6
0	55.4	52.4	68.0

The experimental values are invariably higher than those calculated from the pressure change, which is to be expected as some decomposition had occurred before the initial reading was taken. The discrepancy need not be attributed entirely to this cause as there are other errors due to the conversion of a pressure reading at liquid air temperatures to 0 or 20°. This table may be considered as confirming our assumption that the net reaction is merely the decomposition of ozone and that the decomposition of the chlorine trioxide can be neglected with respect to this reaction. An additional confirmation of the latter fact is obtained from a comparison of the rate of decomposition of the oxide with that of the ozone. In one particular experiment at 0°, dp/dt in the absence of ozone was 0.001 cm. per minute and in the presence of 100 cm. of ozone dp/dt was 0.033 cm. per minute. The magnitude

(2) Bodenstein, Harteck and Padelt, *Z. anorg. Chem.*, **147**, 233 (1925); Schumacher and Stieger, *ibid.*, **184**, 272 (1929).

(3) Allmand and Spinks, *J. Chem. Soc.*, 599 (1932).

(4) Bodenstein, Padelt and Schumacher, *Z. physik. Chem.*, **B5**, 209 (1929).

(5) The oxide was liquid in the presence of a few millimeters pressure of chlorine.

of the effect in the absence of ozone is, of course, a function of the amount of oxide used but this was regulated so as to make the correction negligible, or at least very small.

All of the rate measurements were made with excess of either solid or liquid chlorine trioxide present, so the concentration of this substance could be considered constant throughout a run. There was no evidence that the amount of the oxide present had any influence on the rate except for the small effect due to its decomposition as mentioned above. The initial rates were found to be proportional to the ozone pressure but if any large fraction of the ozone was decomposed the rate constants calculated on the assumption that the reaction was first order with respect to ozone showed a marked trend. It was shown that this effect was due to an inhibiting action by the oxygen formed in the reaction such that the rate could be expressed by the equation

$$\frac{dp}{dt} = k(O_3)/1 + k' \frac{(O_2)}{(O_3)}$$

As an additional test oxygen was admitted to the reaction vessel and the rate decreased as predicted by this law. In order to evaluate k and k' we plotted $(O_3)/(dp/dt)$ as ordinates with $(O_2)/(O_3)$ as abscissa which gives a straight line with the intercept on the ordinate axis equal to $1/k$ and the slope multiplied by the intercept equal to k' . The line marked O_2 in Fig. 1 is a plot of this type.

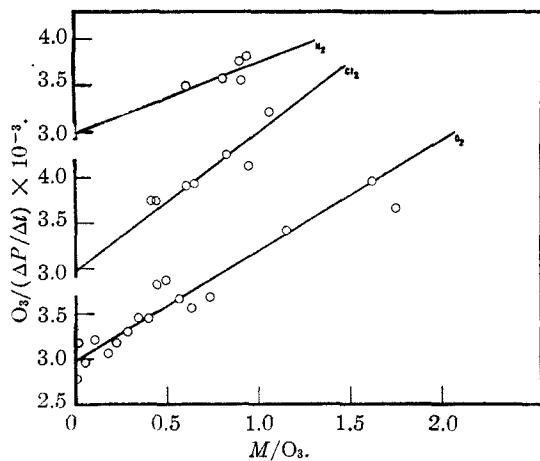


Fig. 1.

The values obtained for k and k' at 0° and also at 20° are tabulated in Table III. The pressures are given in centimeters of sulfuric acid and the constant k is for rates expressed in centimeters of sulfuric acid per minute.

TABLE III
VALUES OF k AND k' . $\frac{dp}{dt} = k(O_3)/1 + k' \frac{(O_2)}{(O_3)}$

Temperature, 0°		
Initial O_3	$k \times 10^4$	k'
83	3.50	0.27
105	3.45	.41
95	3.39	.37
66	3.12	.46
88	3.39	.45
79	3.22	.36
78	3.28	.43
110	3.45	.40
Mean value	3.35	.39
Temperature, 20°		
Initial O_3	$k \times 10^3$	k'
92	4.53	0.38
79	3.92	.48
117	4.24	.46
85	3.88	.42
Mean value	4.14	.435

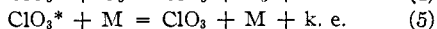
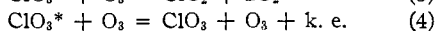
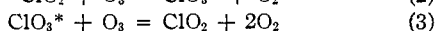
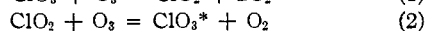
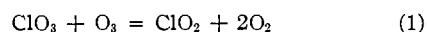
In order to determine whether the action of oxygen is specific or if other gases have a similar effect, several runs were made with nitrogen and chlorine as the added gases. These results are shown in Fig. 1 by the curves marked N_2 and Cl_2 . The value of k with no added gas is, of course, the same whether the gas is N_2 , Cl_2 or O_2 but k' varies slightly. The values which were found at 0° are, for N_2 0.25, O_2 0.39, Cl_2 0.50. Since the change of k' with temperature was found to be very slight with O_2 the experiments with N_2 and Cl_2 were tried only at 0° . The differences between the different gases are so small that they may be attributed to differences in effective diameters and also a slight difference in the efficiency of such collisions as occur.

In view of the work of Bodenstein, Padelt and Schumacher in which the reaction between ClO_3 and O_3 was assumed to occur and a heat of activation calculated, it is of interest to calculate a heat of activation from our data. We cannot use the values of k given in Table III for this purpose as they include a factor depending on the ClO_3 concentration, which is not the same at the two temperatures. In order to eliminate this factor we have made determinations of the vapor pressure of the oxide which are probably not in error by more than 10%. The values are 2.6 mm. of sulfuric acid at 0° and 8.8 mm. at 20° .

The power to which ClO_3 comes into the rate law has not been determined experimentally but in view of the work of Bodenstein, Padelt and Schumacher and also the mechanism to be pre-

sented in the following paragraphs it seems reasonable to assume a first power. If we do this we find that the ratio of the specific rate constants at 20 and 0° is 3.92. This corresponds to a heat of activation of 10.9 k. cal. as compared to 11.8 k. cal. obtained by Bodenstein, Padelt and Schumacher by somewhat indirect means. This agreement is considered to be well within the limits of error of the determinations and therefore in this respect our results may be considered a confirmation of this earlier work.

A mechanism from which our observed rate law may be deduced is represented by the following equations:



In these equations ClO_3^* is used to represent an energy-rich molecule which reacts with ozone much more readily than the normal molecules. One possibility is that it has a peroxide structure which rearranges to the normal structure in reactions (4) and (5). The above mechanism represents a chain process in which the chains are started by (1) and carried on by (2) and (3) until terminated by (4) or (5). Applying the usual methods for deriving the rate law corresponding to the above equations we obtain

$$\begin{aligned} \frac{-d(\text{O}_3)}{dt} &= 2k_1(\text{ClO}_3)(\text{O}_3) + \frac{2k_1k_3}{k_4}(\text{ClO}_3)(\text{O}_3)/1 + \frac{k_5}{k_4} \frac{(\text{M})}{(\text{O}_3)} \\ &= 2k_1(\text{ClO}_3)(\text{O}_3) \left[1 + \left(\frac{k_3/k_4}{1} + \frac{k_5}{k_4} \frac{(\text{M})}{(\text{O}_3)} \right) \right] \end{aligned}$$

This equation reduces to the form of the one found experimentally if k_3/k_4 is much larger than unity, so that the first term may be neglected. Expressed in other words an ozone molecule must react according to (3) more readily than (4). This is not improbable.

The heat of activation which has been calculated from our experimental data is to be attributed to reaction (1), with the possibility of some slight modification due to the reactions (3), (4) and (5). From the fact that k_5/k_4 is independent of temperature within the limits of error of the experiments, we may conclude that these two constants have the same heat of activation, probably zero. Then since k_3 is greater than k_4 the probability is that the heat of activation corresponding to k_3 is either zero or at least very small so that it is probable that the net observed

heat of activation is not appreciably affected by k_3 , k_4 or k_5 . If we knew what fraction of the collisions between chlorine trioxide and ozone molecules which involve an energy equal to the heat of activation are effective in causing reaction we could calculate the chain length. Ordinarily it is assumed that the rate constant is given by $k = se^{-Q/RT}$ in which s is assumed to be equal to the number of collisions, *i. e.*, 10^{11} if the concentrations are expressed in moles per liter and the time in seconds. A simple calculation shows that our observed rate is less than one per cent. of the rate calculated on this basis and therefore s must be considerably less than 10^{11} for the reaction between chlorine trioxide and ozone. The calculations of ClO_3 concentrations made by Bodenstein, Padelt and Schumacher on the assumption that $s = 10^{11}$ gave results much too low and it is quite probable that the actual concentrations in their experiments were not far below the condensation point.

A possible explanation of the discrepancy mentioned in the previous paragraph is that reaction (1) is not a simple bimolecular reaction but occurs on the surface of the reaction vessel. The fact that the observed rate of reaction is independent of the amount of chlorine trioxide is contrary to this view but in order to secure additional evidence we have carried out experiments in which the surface was increased by packing the reaction vessel with glass wool. These experiments showed a slight increase in rate amounting to about 30% at 0° but that may be attributed in part at least to a lack of temperature equilibrium with the bath surrounding the reaction vessel. In any event with this large increase in surface we should find a much larger effect if the reaction were not truly homogeneous.

Summary

It has been shown that one of the processes involved in the chlorine sensitized decomposition of ozone is the formation of chlorine trioxide and the reaction of this compound with ozone. A kinetic study has been made of the latter reaction and the results interpreted in terms of a chain mechanism. The relative efficiencies of chlorine, nitrogen and oxygen in breaking these chains have been found to be of the same order of magnitude. The temperature coefficient of the reaction was found to correspond to a heat of activation of 10.9 k. cal.