Some Remarks on the Decomposition of Ozone Catalyzed by Chlorine

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Bodenstein, Padelt and Schumacher (1.) have studied the decomposition of ozone catalyzed by chlorine. The reaction is a practically homogeneous process, the dimensions and conditions of surfaces and the addition of inert gases exert no influence on the velocity. The reaction starts with an induction period and its intermediate can be frozen in. A very careful spectroscopic search for the absorption of the intermediate failed. Its fractional distillation did not succeed. After a detailed discussion of experimental data Bodenstein, Padelt and Schumacher suggested the following mechanism:

$$1.\ Cl_2 + O_2 = ClO + ClO_2,$$
$$2.\ ClO_2 + O_3 = ClO_3 + O_2,$$
$$3.\ ClO_3 + O_3 = ClO_2 + 2\,O_2,$$
$$4.\ ClO_3 + ClO_3 = Cl_2 + 3\,O_2,$$
$$5.\ ClO + ClO = Cl_2 + O_2.$$

From this scheme the experimentally found velocity equation

$$-\frac{d}{dt}[O_3] = k\,[Cl_2]^{1/2}\,[O_3]^{3/2} \tag{I}$$

is available, with the restriction that the primary (1) and the last (4) reactions, breaking the chain, do not contribute in considerable extent to the velocity. Bodenstein and Schumacher have calculated the single reaction rates from the data of one experiment transitorily frozen in after the induction period.

These statements are also accepted by Hamann and Schumacher (2) in the discussion of their experimental data, although their results differ in many important points from those of Bodenstein, Padelt and Schumacher. The experiments of Hamann and Schumacher yielded essentially greater velocity constants than those of Padelt. The velocity constants depend on chlorine pressure and especially in the case of great chlorine concentration they drop down, even within one experiment. Hamann and Schumacher attribute these deviations to the reactions of ClO. They suggest that in the experiments of Bodenstein, Padelt and Schumacher ClO also reacts with impurities, while in their all-glass apparatus and in their very clean gas ClO can only react in the process ClO + ClO leading to very complicated and irregular reactions, not yet investigated particularly. Furthermore they also assume a reaction between ClO and ozone. The direct consequence of these statements is that the quantum yield in the photochemical decomposition of ozone,

sensitized by chlorine cannot be exactly equal to two as found by Schumacher and Wagner (3). Indeed, Allmand and Spinks, (4, 5) further Heidt, Kistiakowsky and Forbes (6) have found differences in quantum yield amounting to 100—200 per cent. Of course, this annuls the validity of the suggestions of Schumacher and Wagner. To make the reactions of ClO responsible for these deviations, did, however, not succeed. As on the one hand, ClO interacts in all the reactions of chlorine and oxygen compounds and a similar pheno-menon could not be noticed. On the other hand, and this is the main deficiency of the conclusion of Hamann and Schumacher, no reaction of ClO can explain the dependence of the velocity upon the chlorine pressure. Chlorine undoubtedly inhibits the reaction. The chlorine molecules themselves are not capable of exerting this influence, as no inhibitory reaction can be conceived between Cl$_2$ and the other reaction partners. However, the chlorine atom wich can only occur under extremely clean experimental conditions may inhibit the process in reaction:

$$ClO_2 + Cl = Cl_2 + O_2.$$
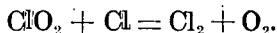
Assuming the presence of chlorine atoms the constants become secondarily independent of the chlorine concentrations. In clean mixtures the ruptures of the chains get also rarer, this explains the increase of the velocity.

In another communication I have dealt (7) with the relation between chloric oxide (ClO) and chlorine trioxide and discussed the replacing of ClO$_3$ by ClO in reaction schemes. Thus the decompo-sition of ozone under the same limiting conditions as by Bodenstein, Padelt and Schumacher, can be described by the following mecha-nism:

$$1. \ Cl_2 + O_3 = ClO + ClO_2,$$
$$2. \ ClO_2 + O_3 = ClO + 2\,O_2,$$
$$3. \ ClO + O_3 = ClO_2 + O_2,$$
$$4. \ ClO + ClO = Cl_2 + O_2.$$

Supplementally we must still postulate the presence of Cl atoms. These can form in different ways. From the hitherto avai-lable data one cannot determine which of the many possible sources deliver them. Considering the circumstances of the reaction, the existence of a thermodynamical equilibrium seems very impro-bable. Let us assume, however, to simplify the calculations, that the chlorine atom concentration is proportional to the square root of the chlorine concentration:

$$Cl = \sqrt{K\,Cl_2}$$

K being only a proportionality factor. This assumption proved to be valid in a wide range of experimental conditions.
Thus the supplementary reactions will be:

$$5. \ Cl + O_3 = ClO + O_2,$$
$$6. \ Cl + ClO_2 = 2\,ClO = Cl_2 + O_2.$$

According to experiences reaction (5) proved to have only a small part in the conversion. Thus at the deduction of the velocity equation the terms of higher order can be neglected. After a great extent of simplification we obtain for the reaction rate the following equation:

$$-\frac{d[O_3]}{dt} = \frac{2k_3\sqrt{\frac{2k_1}{k_4}}[Cl_2]^{1/2}[O_3]^{3/2}}{1+\frac{k_6}{k_2}\sqrt{K}\frac{[Cl_2]^{1/2}}{[O_3]}} \qquad (II.)$$

Recalculating the experiments of Hamann and Schumacher on the base of this equation, we obtain constants without dependence on chlorine concentration and without dropping within one experiment. The effect of this new correction on the velocity equation is especially revealed at experiments with small chlorine concentration, where neither according to (I.), nor to (II.) a drop in constants occurs. A correction of this kind can only be given by a velocity equation of this structure.

Table. 1.

Exp. 44.   T = 50° C.   Cl$_2$ = 20.4 mm
O$_3$ = 104.2 mm   O$_2$ = 6.7 mm

t	O$_3$	k. 10⁵ from (I.)	k corr 10⁴ from (II.)
0	104.2	—	—
14.0	96.4	12.3	1.35
28.5	88.6	13.1	1.44
44.7	80.4	14.5	1.61
59.2	73.8	15.0	1.68
79.4	66.0	14.7	1.67
107.8	57.4	13.9	1.61
138.8	50.0	13.4	1.58
192.0	39.8	14.2	1.72
	0.0	—	

Mean value 1.58

Exp. 21.   T = 50°·   Cl$_2$ = 424.2 mm
O$_3$ = 65.6 mm   O$_2$ = 5.5 mm

t	O$_3$	k. 10⁵ from (I.)	k corr 10⁴ from (II.)
0	65.6	—	—
11.5	58.6	5.83	(0.99)
22.8	51.6	7.56	1.36
35.7	44.4	8.21	1.58
53.7	37.4	7.23	1.52
83.1	28.6	7.76	1.89
155.8	19.4	5.34	1.66
378	14.6	1.52	(0.58)
	0.0	—	

Mean value 1.60

For the value $k_6/k_2 \cdot \sqrt{K} = a$ we obtain 2 to 5, independently of temperature. In consequence of the great experimental errors the ratio of the constants cannot be determined more accurately. These seem to be the greatest at 35° C. Most probably the errors are due to the fact of Hamann and Schumacher not working always uniformly (l. c. 296. p). Sometimes they exhausted the reaction vessel with a water jet pump, and in other cases with a mercury diffusion pump. The degree of exhaustion has a great influence on the reaction rate, as was manifested in experiments of Beawer and Stieger, and Bodenstein and Szabó respectively (8, 9).

The ratio of the constants of the inhibitory and competing reactions is independent of the temperature in agreement with other experimental data. Value a contains also K. We have mentioned above that in respect to chlorine atoms no thermodynamical equilibrium set in. This can be seen from value a. It is too large and K can by no means signify the equilibrium constant of the chlorine atom. The essential meaning of this K must still be interpreted.

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