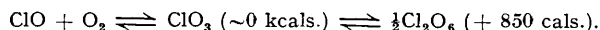## 277. The Relation between Chlorine Oxide (ClO) and Dichlorine Hexoxide.

### By Zoltán G. Szabó.

Examination of the properties of, and rôles played by, the radical chlorine oxide (ClO) and dichlorine hexoxide (Cl_2O_6) shows these substances to be closely related, as indicated by the reactions

$$ClO + O_2 \rightleftharpoons ClO_3 \ (\sim 0 \text{ kcals.}) \rightleftharpoons \tfrac{1}{2}Cl_2O_6 \ (+ \ 850 \text{ cals.}).$$

·ONLY partial success has resulted from the extensive investigations of the photochemical and thermal decomposition of dichlorine monoxide (chlorine monoxide; Cl_2O) and chlorine dioxide (ClO_2), or of the catalysed and chlorine-sensitised decomposition of ozone. These investigations have, however, established some close relations between the reactions of these substances and ·demonstrated that the mechanisms of the reactions of chlorine–oxygen compounds are based on common, fundamental, and simple processes. Discussion of chlorine oxide (ClO) and dichlorine hexoxide (Cl_2O_6) from this generalised viewpoint shows a close relation between them and ·eliminates many discrepancies inherent in the older mechanisms.

The Radical ClO.—The existence of a radical ClO was postulated in the early work and many ·of its properties were determined. Chlorine oxide (ClO) is produced in the reaction of dichlorine ·monoxide with chlorine atoms (Finkelnburg, Schumacher, and Stieger, *Z. physikal. Chem.*, 1932, *B*, **15**, 127) :

$$Cl + Cl_2O = ClO + Cl_2 + 14 \text{ kcals.}$$
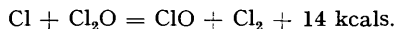
·and in that of chlorine dioxide and oxygen atoms (data recalculated from those of Finkelnburg) :

$$O + ClO_2 = ClO + O_2 + 48 \text{ kcals.}$$
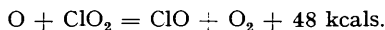
Both reactions proceed without inhibition and play an important part in the chains formed ·during decomposition of these gases. Thus ozone and chlorine atoms produce ClO, also without any great activation energy, as follows, the thermal value being that recalculated by use of ·ClO = Cl + O − 50 kcals. (Finkelnburg *et al.*, *loc. cit.*) from Goodeve and Marsh's data (*J.*, 1939, 1332) :

$$Cl + O_3 = ClO + O_2 + 25 \cdot 5 \text{ kcals.}$$

Photochemical dissociation of dichlorine monoxide also affords ClO : the first maximum ·(at 6250 A.) in the spectrum of dichlorine monoxide corresponds to an energy of 45·5 kcals./mole, ·whilst the reaction $Cl_2O \longrightarrow ClO + Cl$ is endothermic to the extent of 43 kcals./mole (Finkelnburg *et al.*, *loc. cit.*).

In the decomposition of chlorine dioxide the primary reaction (occurring on the wall of the ·vessel) which is capable of propagating chains is, according to Schumacher and Stieger (*Z. physikal. Chem.*, 1930, *B*, **7**, 363) :

$$ClO_2 = ClO + O − 70 \text{ kcals.}$$
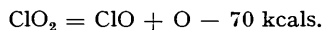
Experiment shows that ClO is perhaps a little more inert but nevertheless constitutes the most important propagator of these chains. Its low activity, compared with the chlorine atom, is to be ascribed to the activation energy necessary for its reactions with molecules. Its decomposition ·thus requires activation energy and produces a notable heat of reaction (Finkelnburg *et al.*, *loc. cit.*) :

$$2ClO = Cl_2 + O_2 + 74 \text{ kcals.}$$
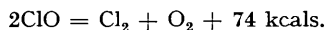
·or, when activation is successful :

$$2ClO = 2Cl + O_2 + 17 \text{ kcals.}$$
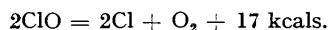
In the latter case there is no breach of the chain but, instead, two ClO radicals which disappear produce two chlorine atoms which maintain a steady concentration of chain propagators, as Beaver and Stieger (*Z. physikal. Chem.*, 1931, *B*, **12**, 93) found for the decomposition of dichlorine monoxide.

In the decomposition of dichlorine monoxide and chlorine dioxide, ClO doubtless plays an important rôle. However, its effect on the chlorine-sensitised or catalysed decomposition of ozone was for long unexplained, so that many discrepancies observed in these reactions have been ascribed to ClO (Hamann and Schumacher, *ibid.*, 1932, *B*, **17**, 293). Attempts to make ClO responsible for these anomalies failed, however, since similar anomalous behaviour was not observed in other processes although ClO occurs in every reaction of chlorine–oxygen compounds. The anomalies, in fact, are due to the chlorine atoms.

The first mechanism suggested for the chlorine-catalysed decomposition of ozone was that of Bodenstein, Padelt, and Schumacher (*ibid.*, 1929, *B*, **5**, 209), who suggested that the chains are propagated by the reaction

$$ClO_2 + O_3 = ClO_3 + O_2$$
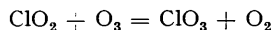
This appeared to be supported by the formation of dichlorine hexoxide from chlorine and ozone or, better, from chlorine dioxide and ozone at low temperatures. The latter is the most convenient method of preparing dichlorine hexoxide (Schumacher and Stieger, *Z. anorg. Chem.*, 1929, **184**, 272). It was assumed by Bodenstein and his collaborators (*ibid.*, 1925, **147**, 233; *Z. physikal. Chem.*, 1929, *B*, **5**, 233) that dichlorine hexoxide was formed by a readily occurring dimerisation; this was investigated in detail by Goodeve and his collaborators (*Trans. Faraday Soc.*, 1936, **32**, 790) by measurement of magnetic susceptibilities, who found the dissociation energy $Cl_2O_6 = 2ClO_3$ to be -1700 ± 500 cals. The next step in Bodenstein's scheme was continuation of the chain, thus :

$$ClO_3 + O_3 = ClO_2 + 2O_2$$
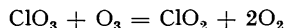
and the chain ends by the reaction

$$2ClO_3 = Cl_2 + 3O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

This suggestion, that ClO_3 is a chain propagator, was accepted also by later authors, albeit more or less modified (Allmand and Spinks, *J.*, 1932, 599; Byrns and Rollefson, *J. Amer. Chem. Soc.*, 1934, **56**, 364, 2245), but Norrish and Neville (*J.*, 1934, 1864) rejected it and proposed instead a chain mechanism involving ClO. From the viewpoint of reaction kinetics Byrns and Rollefson's most important result was that two forms of chlorine trioxide molecules exist, differing in reactivity, and this concept will be included in our later discussion of reactions which occur by way of ClO_3 or Cl_2O_6.

Although dichlorine hexoxide is found in traces in this and other reactions, its formation is not sufficient proof that it is an intermediate product. The most important arguments against this are the following. (*a*) All the reactions occur at high temperatures, at which the stability of ClO_3 is very doubtful. (*b*) Hamann and Schumacher (*loc. cit.*) were unable to identify any of the intermediates which should have been found spectroscopically—ClO_3 has a large absorption and should have been thus found. (*c*) Dichlorine hexoxide is stable in the liquid state, so that chain termination in Bodenstein's scheme must occur according to equation (*A*) above. This equation cannot, however, possibly represent the reaction, for it would demand the fourth order for the reverse reaction which must occur according to the principle of microscopic reversibility (Bodenstein, " Handbuch der Katalyse," Springer Verlag, Vienna, 1941, Vol. I, p. 315). (*d*) Byrns and Rollefson's assumption of an energetically distinguished molecule ClO_3* refers, as mentioned above, not to a simple activation in the gas-kinetic sense, but to a catalytic reaction with an equally catalysed reverse reaction which deactivates the molecule; to distinguish thus between identical molecules appears a little forced.

On the other hand, in experiments in which the reaction mixture was frozen and later warmed again (Beaver and Stieger; Schumacher and Stieger; Bodenstein, Padelt, and Schumacher, *locc. cit.*) the induction period which could be very accurately measured at the beginning of the experiment was either absent or present only to a very small extent. To explain this phenomenon we must assume the presence of a more stable intermediate than the ClO radical, Cl, or O.

Chlorine dioxide can be shown to be present in each of the reactions. It also is an intermediate which could be frozen out. However, it can on no account be the intermediate discussed above, for there is an induction period in its own decomposition.

Some other intermediate must exist and, since the same behaviour is observed in all the

reactions, it must be common to them all. As this was already suggested by Norrish and Neville for the special case of ozone (*loc. cit.*), every reaction scheme embodying ClO_3 as intermediate can be written with ClO instead. Thus the reactions proceed by way of ClO and of ClO_3 or Cl_2O_6 only at low temperatures, the appropriate equation being

$$ClO + O_2 \rightleftharpoons ClO_3 \rightleftharpoons \tfrac{1}{2}Cl_2O_6$$
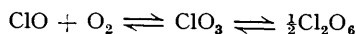
Since ClO occurs in all reactions of chlorine–oxygen compounds, the common intermediate which can be frozen can be no other than ClO or Cl_2O_6.

Freezing the various reaction mixtures gave different amounts of dichlorine hexoxide. This is explicable on the assumption of different concentrations of ClO in the different reaction mixtures. The concentration is notably smaller in the decomposition of dichlorine monoxide or chlorine dioxide than in the reaction of ozone with chlorine or of dichlorine monoxide. The yield of dichlorine hexoxide is also limited by the fact that its formation from ClO and oxygen ceases when the ClO is consumed as no more ClO can be formed at the low temperature of the frozen mixture. On the other hand, in the production of dichlorine hexoxide from ozone and chlorine or from chlorine dioxide the reactions leading to ClO are all primary reactions which occur at low temperature and thus uninterruptedly supply ClO.

The existence of such intermediates which can be frozen out is evidence of the reaction $ClO + O_2 \rightleftharpoons ClO_3$. However, there are also other facts which strongly support this view, particularly the properties of dichlorine hexoxide and ClO_3 (Goodeve and Richardson, *J.*, 1937, 294).

*Dichlorine Hexoxide.*—Dichlorine hexoxide is a dark red liquid; its freezing point ($3.50° \pm 0.05°$) can be considerably lowered by presence of impurities and decomposition products. The liquid has strong absorption throughout the region from *ca.* 6000 A. to the limit 2000 A. The absorption of the gaseous oxide is continuous, with two maxima, one at 2780 A. and the other beginning at 2170 A. The continuous nature of the spectrum of the gas indicates that the molecule dissociates with absorption of a light quantum. We showed above that the heat of dissociation of the hexoxide to the trioxide is *ca.* 1.5 kcals., so that equilibrium in the gaseous state lies entirely on the side of ClO_3.

The second and more interesting dissociation, $ClO_3 \rightleftharpoons ClO + O_2$, is almost thermoneutral, as is readily seen from the equations,

$$2ClO = Cl_2 + O_2 + 74 \text{ kcals.}$$
$$2ClO_3 = Cl_2 + 3O_2 + (74 \pm 4) \text{ kcals.}$$
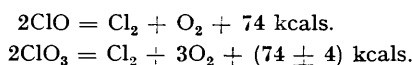
The former heat of reaction was calculated by Finkelnburg, Schumacher, and Stieger (*loc. cit.*); the latter was measured calorimetrically by Goodeve and Marsh (*loc. cit.*). These values surely contain an experimental error, but this is certainly not large enough to remove the reaction $ClO_3 \rightleftharpoons ClO + O_2$ far from thermoneutrality. Thus no great obstacle exists to the building up of ClO and ClO_3 concentrations.

The reactions of dichlorine hexoxide have not been thoroughly studied. Doubtless it reacts with ozone. Byrns and Rollefson found that the reaction is inhibited by foreign gases which deactivate the energy-rich molecules capable of propagating the chain. On the other hand, Norrish and Neville observed inhibition only by chlorine and oxygen. We showed above that the mechanism of chlorine-catalysed decomposition of ozone can be postulated with ClO instead of ClO_3. It is clear that Byrns and Rollefson's activated molecule ClO_3^* can be replaced by ClO. Norrish and Neville interpreted the inhibiting action of chlorine and oxygen as follows, on the assumption that the chlorine atom was a chain propagator :

$$Cl + O_2 = ClO_2 \qquad\qquad ClO_2 + O_3 = ClO_3 + O_2$$
and
$$Cl + Cl_2 = Cl_3 \qquad\qquad Cl_3 + O_3 = ClO_2 + Cl_2$$
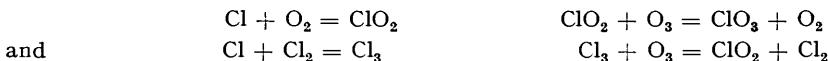
Thus ClO_3 was formed and this broke the chain.

On the basis of the views reported above, the inhibiting action of oxygen and chlorine cannot be of the same nature. In Hamann and Schumacher's experiments chlorine caused inhibition where oxygen was totally without effect. This can be explained in the sense that in these experiments at higher temperatures (35—50°) the equilibrium $ClO + O_2 \rightleftharpoons ClO_3$ was shifted entirely to the left, so that the reactivity of ClO was retained whilst inhibition by chlorine occurred. Meanwhile it cannot be decided whether this inhibition by chlorine—on the assumption that chlorine dioxide is also a chain propagator—occurs by the reaction $Cl + ClO_2 = Cl_2 + O_2$ or by the reactions envisaged by Norrish and Neville utilising Cl_3.

Byrns and Rollefson (*loc. cit.*) and Goodeve and Richardson (*loc. cit.* and *Trans. Faraday Soc.*, 1937, **33**, 354) found the activation energy for the decomposition of dichlorine hexoxide to be *ca.* 22 kcals. Bodenstein and his collaborators calculated a heat of activation of 11—22 kcals. for the reaction $2ClO_3 = Cl_2 + 3O_2$. Clearly the latter value represents the activation energy of the reaction $2ClO = Cl_2 + O_2$ in the experimental conditions used by these authors. The discrepancy is easily eliminated by the consideration that the value 22 kcals. includes the heat of evaporation which amounts to 9·5 kcals. (Goodeve and Richardson, *J.*, 1937, 294).

Treatment of the mechanisms of reactions of oxygen–chlorine compounds on the lines developed above will assuredly lead to further simplifications and explanations.