283. *The Heat of Decomposition of Chlorine Trioxide, and the Energy of the Oxygen–Chlorine Bond.*

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A value of $\Delta H_{15°} = -37 \pm 2$ kg.-cals./mol. has been obtained for the heat of the reaction $ClO_3 \rightarrow \frac{1}{2}Cl_2 + 1\frac{1}{2}O_2$, and the heats of decomposition of all the oxides of chlorine are now known. A value of 52 ± 1 kg.-cals. has been calculated for the normal 2-electron O–Cl bond energy in the chlorine oxides. The dichlorine monoxide molecule is weakened to the extent of about 10 kg.-cals. by a strain in the oxygen angle, and the dichlorine heptoxide molecule is weakened to a slightly greater extent. The strengthening influence of the odd electron in chlorine tri- and di-oxide has been calculated to be about 11 and 15 kg.-cals. respectively. It has been deduced that the heat of decomposition of ClO into atoms is about 67 kg.-cals. Applications of the thermochemical data to the kinetics of the reactions of the oxides of chlorine are discussed.

CHLORINE trioxide is involved as an intermediate product in many of the thermal and photochemical decomposition reactions of the oxides of chlorine. It is also formed in the thermal and photochemical reactions between chlorine and ozone, and in the thermal reaction between chlorine dioxide and ozone. A knowledge of its heat of decomposition is of importance in understanding the kinetics of these reactions.

The oxides of chlorine are difficult subjects for calorimetric measurements, as their decomposition is not easily controlled and they react vigorously with all tap lubricants, mercury, etc. The application of a new calorimetric technique to measurements of the heat of decomposition of dichlorine heptoxide has recently been described (Goodeve and Marsh, J., 1937, 1161) and this method has now been applied to chlorine trioxide.

Preparation of Chlorine Trioxide.—This was prepared by the reaction of dilute streams of gaseous ozone and chlorine dioxide as described by Goodeve and Richardson (J., 1937, 294) (cf. Schumacher and Stieger, *Z. anorg. Chem.*, 1929, **184**, 272). The design of the reaction chamber was now modified, however, so that the reactants mixed in a bulb at the top, at room temperature, the product being collected at the bottom of the trap which was cooled in melting ice. In this way the yield was considerably increased and the formation of chlorine trioxide beyond the reaction chamber was avoided.

EXPERIMENTAL.

Owing to the low vapour pressure of chlorine trioxide, several minor modifications of the apparatus used in the calorimetric experiments on the heptoxide were necessary in order to obtain a sufficiently rapid rate of flow of the gaseous oxide. The Gaede pump was supplemented by a mercury diffusion pump, and the diameter of all tubing increased, and the length decreased, wherever possible. The diameter of the jet in the decomposition chamber was increased to about 2 mm., and the two sand plugs removed. These alterations, although not sufficient to give as rapid a rate of decomposition as in the experiments on the heptoxide, provided the maximum rate of flow compatible with complete decomposition of the trioxide. In order to avoid appreciable decomposition of the chlorine trioxide in passing through tubes, the required amount was distilled into a short U-tube close to the decomposition chamber just before an experiment and purified by fractional distillation.

Since the heat effects measured in these experiments were less than in the decomposition of the heptoxide, an accurate knowledge of the changes in wattage of the filament during the course of the decomposition was increasingly important. After some preliminary experiments the ammeter and voltmeter previously used were supplemented by galvanometers in potentiometer circuits designed to give the required accuracy.

During the course of these experiments it was observed that the resistance of the platinum filament was always slightly higher at the end of the experiment than at the beginning. This may have been due to distillation of platinum under the high vacuum conditions or to attack of the platinum by chlorine or chlorine trioxide.

The theory developed in the previous paper showed that the sum of the integrals of the heat effects occurring in the calorimeter between time $t = 0$ and $t = \infty$ was equal to zero, since the calorimeter returned to its initial equilibrium temperature. Owing to the permanent changes in the resistance (and hence in the wattage) of the filament during the present experiments, the sum of the integrals is now equal to $C(T_e' - T_e)$, where C is the heat capacity of the calorimeter, and T_e' and T_e are the final and the initial equilibrium temperature respectively. Hence

$$q + \int_0^\infty \frac{W - W_e}{4\cdot18}\, dt - k \int_0^\infty (T - T_e)dt = C(T_e' - T_e)$$

or

$$q = k \int_0^\infty \left[(T - T_e) - \frac{(W - W_e)}{4\cdot18k} \right] dt + C(T_e' - T_e) \quad . \quad . \quad . \quad . \quad (1)$$

q is the heat produced by the chemical reaction, and k a constant determining the rate of removal of heat and equal to $c_w dm/dt$, where c_w is the specific heat of water and dm/dt its rate of flow through the cooling coil; T is the calorimeter temperature, W the wattage of the filament at any instant during the experiment, and W_e the initial equilibrium value.

The integral is simply the area enclosed by the plots of $(W - W_e)/4\cdot18k$ and $(T - T_e)$ against time. As shown in the previous paper, it is convenient to divide the graph into two parts at a time chosen after the reaction had ceased and the wattage become steady. If the temperature at this instant is T_0 the value of A_2 (see previous paper) is $(T_0 - T_e')C/k$. Therefore equation (1) becomes

$$q = k[A_1 + (T_0 - T_e')C/k] + C(T_e' - T_e) = kA_1 + C(T_0 - T_e) \quad . \quad . \quad . \quad (2)$$

4 s

It is seen that the method used in the previous paper for calculating the heat evolved in the chemical reaction is still applicable when permanent changes in the wattage of the filament produce a change in the final equilibrium temperature and that the latter need not be known.

The value of c_w was taken as unity; dm/dt was measured directly and was generally close to 0·25 g./sec. A blank run confirmed that the value of k obtained directly was equal to that calculated from the logarithmic function of the cooling curve (see previous paper). The wattage was about 2 volt-ampères, and the heat capacity about 300 cals./degree.

Results.—The results are summarised in Table I. The high chlorine analyses were due to incomplete decomposition, with the production of small amounts of chlorine dioxide (which
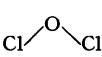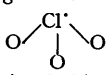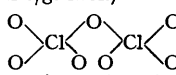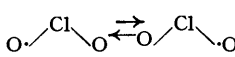
TABLE I.

q.	ClO₃ decomposed, millimols., from O₂.	from Cl₂.	ΔH, kg.-cals./mol., from O₂.	q.	ClO₃ decomposed, millimols., from O₂.	from Cl₂.	ΔH, kg.-cals./mol., from O₂.
8·95	0·238	0·254	−37·6	13·48	0·342	—	−39·4
15·30	0·408	0·426	−37·5	10·62	0·302	0·305	−35·2
11·14	0·317	0·315	−35·2	13·02	0·293	0·297	(−44·4)
11·90	0·325	0·341	−36·6			Mean	−37

liberates *five* equivalents of iodine). Values of ΔH, based on the oxygen analyses, can be shown by calculation to have only small errors arising from this incomplete decomposition because the ratio of the heat of the reaction, $ClO_3 \rightarrow ClO_2 + \frac{1}{2}O_2$, to that of the complete reaction is nearly the same as the ratio of the oxygen produced in the two cases, *i.e.*, 1 : 3. The cause of the high value in the last experiment is not known, and account has not been taken of this value in the average.

Possible sources of error have already been suggested in the paper on the heptoxide. In the present experiments, the slower rate of heat production and the smaller quantities of oxide decomposed have inevitably led to an increase in the limits of error. The changes in heat conductivity, due to the increase in the gas pressure during the reaction, caused changes in the amount of heat contained in the filament and its capillary and a distortion of the shape of the temperature–time curve from that shown in the previous paper. These changes balance out except for the small effect due to the permanent change in wattage. The error introduced here was negligible, since the change in wattage was very small. An examination of these limits of error led to the conclusion that they are not greater than those indicated by the results in Table I. The value of $\Delta H_{15°}$ for the reaction $ClO_3 \rightarrow \frac{1}{2}Cl_2 + 1\frac{1}{2}O_2$ is therefore -37 ± 2 kg.-cals., or $\Delta U_{15°} = -37·6 \pm 2$ kg.-cals.

The Energy of the Oxygen–Chlorine Bond.—From the heats of decomposition of the oxides of chlorine and the dissociation energies (Jevons, "Band Spectra of Diatomic Molecules," 1932) of oxygen ($\Delta U = 117·3$ kg.-cals.) and chlorine ($\Delta U = 57$ kg.-cals.), the energies of dissociation of the chlorine oxides into their constituent atoms, *i.e.*, the total bond energies, have been calculated (see Table II). Strictly, the total bond energy should be calculated from ΔU at 0° K., but as the specific heats are not known, this is not possible. The values given in Table II are therefore about 1% too high.

TABLE II.

(All energies are in kg.-cals./g.-mol.)

Oxide :	$Cl{\diagup}^{O}{\diagdown}Cl$	$O{\diagup}\overset{\overset{Cl\cdot}{\vert}}{\underset{O}{}}{\diagdown}O$ (probably non-planar).	$\underset{O}{\overset{O}{}}{\diagdown}Cl{\diagup}\overset{O}{\underset{O}{}}{\diagdown}Cl{\diagup}\overset{O}{\underset{O}{}}$ (non-planar).	$O{\diagdown}^{Cl}\!\!{\diagup}O{\overset{\rightarrow}{\leftarrow}}O{\diagup}^{Cl}{\diagdown}O$
ΔH	−21·7	−37·0	−63·4 †	−26·6 *
ΔU	−22·0	−37·6	−65·5	−26·9
Total bond energy	+93·7	+167·0	+402·0	+119·0
Average bond energy...	47·0	55·6	50·3	59·5
r_e(O–Cl), A	1·71	—	—	1·57
Total weakening	10	—	14	—
Total strengthening ...	—	11	—	15

* Wallace and Goodeve, *Trans. Faraday Soc.*, 1931, **27**, 648.
† Goodeve and Marsh, J., 1937, 1161.

Division of the total bond energy by the number of bonds gives the average oxygen–

chlorine bond energy, and it is seen that this is different for each compound. In what follows these differences are attributed to two causes.

The oxygen angle in dichlorine monoxide (111° $\pm$ 2°) is equal to that in the ethers (111° $\pm$ 4° for dimethyl ether) and greater than that in water and difluorine monoxide (105°). The larger angles in dichlorine monoxide and dimethyl ether are attributed by Sutton and Brockway (*J. Amer. Chem. Soc.*, 1935, **57**, 473) to steric repulsion between the chlorine atoms and methyl groups respectively. This is supported by the fact that the Cl–Cl distance (2·82 A) is less than the distance of nearest approach of two unbonded chlorine atoms in solid benzene hexachloride and other crystalline chlorine compounds (3·7 A). The total bond energy of dichlorine monoxide is thus the sum of two 2-electron bonds minus a weakening effect due to repulsion between the chlorine atoms. One concludes, therefore, that the normal 2-electron O–Cl bond energy is *greater than* 47 kg.-cals./mol.

In chlorine trioxide the oxygens are held to the chlorine mainly by 2-electron bonds, although in this case both the electrons in each bond come originally from the chlorine atom. There is, however, an odd electron which may contribute to the whole binding energy of the molecule, and we may conclude that the normal 2-electron bond energy is somewhat *less than* the average bond energy, 55·6 kg.-cals. That this odd electron does not contribute much binding energy may be concluded from the fact that it is available to cause association to dichlorine hexoxide, although the energy of the associating bond is low, about 2 kg.-cals. (Farquharson, Goodeve, and Richardson, *Trans. Faraday Soc.*, 1936, **32**, 790).

Dichlorine heptoxide has six 2-electron bonds, apparently quite unperturbed, and two strained, for the same reason as in dichlorine monoxide. The average bond energy, 50·3 kg.-cals., is therefore nearer the correct one than either of the previous ones. However, from Fonteyne's calculation (*Natuurwetensch. Tijds.*, 1938, **20**, 275) that the angle at the central oxygen is 128°, we can deduce that the energy of each of the central bonds is less than the 47 kg.-cals. found for dichlorine monoxide. We will tentatively assign a value of 45 kg.-cals. to these bonds, assuming a maximum error of 3 kg.-cals. On this assignment the six normal 2-electron bonds have each an energy of 52 $\pm$ 1 kg.-cals.

Chlorine dioxide belongs to the class of *stable* odd-electron molecules and there is no evidence for its association to dichlorine tetroxide (Goodeve and Young, unpublished results). Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 3225) has explained the stability of certain odd-electron molecules on the basis of a three-electron bond. Brockway (*Proc. Nat. Acad. Sci.*, 1933, **19**, 303) has shown that chlorine dioxide satisfies the conditions necessary for the existence of such a bond. The resulting increased bond strength is reflected in the closer equilibrium separation, r_e.

On the basis of 52 kg.-cals. for the normal oxygen–chlorine bond, the total weakening effect of steric repulsion and total strengthening effect of the odd electron in the respective cases have been calculated and are shown in the lower part of Table II. There are, of course, other methods of approach and other possible assignments, but the one chosen appears to lead to the most reasonable results. It is to be noticed that the total strengthening, 15 kg.-cals., is less than that predicted by Brockway.

Chlorine Oxide, ClO.—Since this oxide has been postulated as an intermediate in many of the reactions of the oxides of chlorine, a knowledge of its heat of formation would be of great assistance. There is good reason to believe from the predissociation spectra of chlorine dioxide that the heat of the reaction, ClO $\rightarrow$ Cl + O, is considerably greater than 43 kg.-cals. In order to apply the above value of 52 kg.-cals. to this compound, it is first necessary to determine whether or not the odd electron increases the bond strength as in chlorine dioxide. There must be resonance between the structures (I) and (II) for the same reasons as given by Brockway for chlorine dioxide, and therefore the odd electron should lead to an increase in bond strength. This may be compared with a parallel case; the bond strength in nitric oxide is much greater than it is in nitrogen dioxide (the odd electron in the former is anti-bonding in the sense that if it is removed a stronger bond can be formed). It is rather difficult to assess the value of the increase in the chlorine oxide bond strength until more is known about the electronic structure, but it is probably

$$\overset{..\ \ ..}{:\text{Cl}:\text{O}:}\qquad \overset{\overset{+}{.}\ \ \overset{-}{..}}{:\text{Cl}:\text{O}:}$$

(I.) (II.)
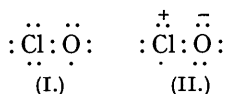
of the same order of magnitude as the total effect in the dioxide (*i.e.*, 15 kg.-cals.). The heat of formation of chlorine oxide from its atoms is therefore about 67 kg.-cals.

The Reactions of the Oxides of Chlorine.—All the oxides of chlorine decompose at room temperature and are very reactive to many compounds, and for this reason have frequently formed the subject of investigations in reaction kinetics. They also in general react photo-chemically. It is now possible to apply the above data to see whether or not the many reaction mechanisms put forward are energetically possible.

As the binding energy of the oxygen molecule is more than twice the normal O–Cl bond energy, reactions such as

$$ClO_3 \longrightarrow ClO + O_2; \quad \Delta U = -17.3 \text{ kg.-cals.} \quad . \quad . \quad . \quad . \quad (1)$$
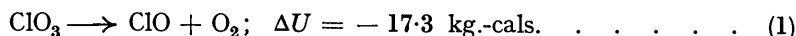
are exothermic. The odd-electron contribution in chlorine dioxide, however, makes the reaction

$$ClO_2 \longrightarrow Cl + O_2; \quad \Delta U = +1.7 \text{ kg.-cals.} \quad . \quad . \quad . \quad . \quad (2)$$
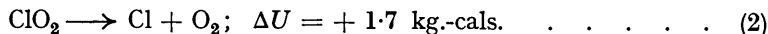
slightly endothermic. Although the energy of activation, E, must, in this case, be greater than ΔU, as a rearrangement of the bonds occurs, reaction (2) probably takes place at room temperature and certainly in preference to

$$ClO_2 \longrightarrow ClO + O; \quad E = \Delta U = +52 \text{ kg.-cals.} \quad . \quad . \quad . \quad . \quad (3)$$
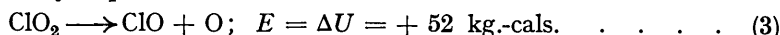
Schumacher and Stieger (*Z. physikal. Chem.*, 1930, **B, 7**, 363) favoured reaction (3) as against (2).

On the other hand the reaction

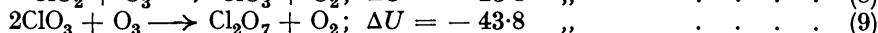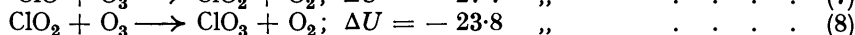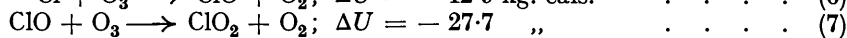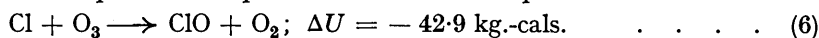$$Cl_2O \longrightarrow ClO + Cl; \quad E = \Delta U = +26.6 \text{ kg.-cals.} \quad . \quad . \quad . \quad . \quad (4)$$
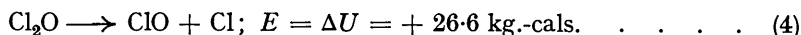
can proceed at room temperature in preference to

$$Cl_2O \longrightarrow Cl_2 + O; \quad E > \Delta U = +36.6 \text{ kg.-cals.} \quad . \quad . \quad . \quad . \quad (5)$$
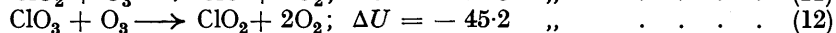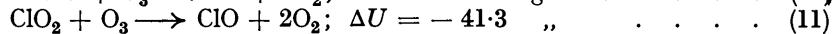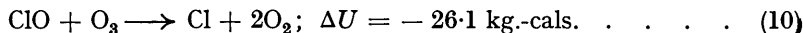
This oxide, when pure, does not explode even on sparking (Wallace and Goodeve, *Trans. Faraday Soc.*, 1931, **27**, 648), and therefore presumably reaction (4) is inefficient in starting chains.

The reactions with ozone form an interesting group. The extra oxygen atom in ozone is held on by only 24.2 kg.-cals. compared with 52 kg.-cals. when held to chlorine, and thus ozone can readily oxidise chlorine and its oxides. All the following reactions are known to occur when chlorine is photo-decomposed into atoms in the presence of ozone.

$$Cl + O_3 \longrightarrow ClO + O_2; \quad \Delta U = -42.9 \text{ kg.-cals.} \quad . \quad . \quad . \quad (6)$$
$$ClO + O_3 \longrightarrow ClO_2 + O_2; \quad \Delta U = -27.7 \quad ,, \qquad . \quad . \quad . \quad (7)$$
$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2; \quad \Delta U = -23.8 \quad ,, \qquad . \quad . \quad . \quad (8)$$
$$2ClO_3 + O_3 \longrightarrow Cl_2O_7 + O_2; \quad \Delta U = -43.8 \quad ,, \qquad . \quad . \quad . \quad (9)$$

The large heat evolved may appear in the oxide of chlorine product to an extent sufficient to cause it to decompose according to reactions (1) or (2). The effect of the oxides of chlorine in sensitising the decomposition of ozone has been explained by reactions (6)—(9) occurring along with

$$ClO + O_3 \longrightarrow Cl + 2O_2; \quad \Delta U = -26.1 \text{ kg.-cals.} \quad . \quad . \quad . \quad (10)$$
$$ClO_2 + O_3 \longrightarrow ClO + 2O_2; \quad \Delta U = -41.3 \quad ,, \qquad . \quad . \quad . \quad (11)$$
$$ClO_3 + O_3 \longrightarrow ClO_2 + 2O_2; \quad \Delta U = -45.2 \quad ,, \qquad . \quad . \quad . \quad (12)$$

The same mechanism can explain the high quantum efficiency in the chlorine-photo-sensitised reaction (Allmand and Spinks, *J.*, 1931, 1652; 1932, 599).

The thermal reaction between chlorine and ozone, which is mainly catalytic, was studied by Bodenstein and his co-workers (*Z. Elektrochem.*, 1913, **19**, 836; *Z. anorg. Chem.*, 1925, **147**, 233; *Z. physikal. Chem.*, 1929, **B, 5**, 209), and later by Hamann and Schumacher (*ibid.*, 1932, **B, 17**, 293) and Norrish and Neville (*J.*, 1934, 1864). All authors agree that the initiating reaction is likely to be

$$Cl_2 + O_3 \longrightarrow ClO + ClO_2; \quad \Delta U = +12.5 \text{ kg.-cals.} \quad . \quad . \quad . \quad (13)$$
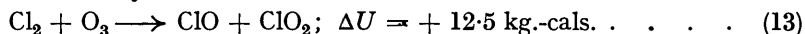
This is followed by reactions (6)—(12). The energy of activation will, however, be much greater than the energy change here calculated, as there is considerable spatial rearrangement

of bonds. On the other hand, ozone with an energy of activation of 24·2 kg.-cals. can produce oxygen atoms. These can start the reactions (6)—(12) by first reacting thus

$$Cl_2 + O \longrightarrow ClO + Cl; \quad \Delta U = -10 \text{ kg.-cals.} \quad . \quad . \quad . \quad . \quad (14)$$

The heats of reaction will be useful in the next stage in the interpretation of these reactions, which involves a deduction of the energies of activation from the structural changes and the force constants of the molecules involved. The necessary data are at present only partly known.

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