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Halogen-Catalyzed Decomposition of N₂O and the Role of the Hypohalite Radical*

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It is shown that the Cl₂ catalyzed decomposition of N₂O cannot be explained by a nonchain reaction but is consistent with a Cl atom chain in which Cl atoms are regenerated by the reactions,

$$2Clo \rightarrow Cl - 0 - 0 + Cl$$

and by followed by

 $ClO-N_2O \rightarrow N_2+Cl-O-O$

Cl-O-O+M-Cl+O2+M

It is proposed that the peroxy radical Cl-O-O is the unstable intermediate responsible for the high efficiency observed for O2 in catalyzing the recombination of Cl atoms. It is also proposed that at low temperatures O_2 should be an efficient catalyst for the generation of Cl atoms via the reaction $O_2+Cl_2 \rightarrow$ O-O-Cl+Cl. The peroxy ClOO species is shown to be a reasonable one to account for the high-rate constant observed for reaction 4' and for the chain decompositions of Cl₂O and OClO. Its thermodynamic properties are estimated as $\Delta H_f^{0} = 21 \pm 2$ kcal, $S_f^{0} = 61$ cal/mole - °K, with a bond-dissociation energy, $D(Cl-OO) = 8 \pm 2$ kcal.

AUFMAN et al.¹ have recently shown that the the calculation of $K_{eq} = k_1/k_2$, then the rate of formation halogen-catalyzed decomposition of N₂O can be described by the rate law:

$$-d(\mathbf{N}_{2}\mathbf{O})/dt = k_{c}(\mathbf{N}_{2}\mathbf{O})(X)_{\mathrm{eq}}$$
(A)

where $(X)_{eq}$ is the concentration of halogen atoms calculated (from independent thermal data) to be in equilibrium with halogen molecules under the experimental conditions.

To account for this rate law they proposed the following mechanism:

$$Cl_{2}+M \underset{2}{\overset{1}{\underset{2}{\longrightarrow}}} 2Cl+M$$

$$Cl+N_{2}O \overset{3}{\xrightarrow{}} ClO+N_{2}$$

$$2ClO \overset{4}{\xrightarrow{}} Cl_{2}+O_{2}$$

which will yield the above rate law A, only if it is assumed that the rate of reaction 2 is considerably faster than the rate of reaction 3.

This scheme further requires that the rate of N₂O consumption by 3 not exceed the rate of Cl atom production by 1. Under a typical set of experimental conditions however we find from the authors' data at $927^{\circ}K^{1}$ that $R(N_{2}O) = -d(N_{2}O)/dt = 0.130$ mm/min. If we use the values of k_2 obtained from studies on the recombination of Br atoms² and spectroscopic data³ for

¹ Kaufman, Gerri, and Pascale, J. Chem. Phys. 24, 32 (1956). ² See, for example, H. B. Palmer and D. F. Hornig, J. Chem. Phys. 26, 98 (1957). We have used a value of $k_2=3\times10^9$ l²m⁻² sec⁻¹.

of Cl atoms is given by

$$d(Cl)/dt = R(Cl) = 2k_1(Cl_2)(M) = 2K_{eq}k_2(Cl_2)(M)$$
 (B)

which gives at 927°K, R(Cl)=0.0238 mm/min so that $R(N_2O)/R(Cl) = 5.5$ at 927°K. We conclude that unless the rate constant for the recombination of Cl atoms is considerably faster than that for Br atoms, the above homogeneous scheme cannot account for the rapid destruction of N₂O molecules.

The discrepancy between the rate law and the above scheme is not however a factor of 5.5 but actually much larger. This follows from the condition mentioned above, that in order for the rate law A to be derived from the scheme, reaction 2>>reaction 3, or $R(N_2O) \ll R(Cl)$. The experimental data seem good enough to set limits⁴ $R(N_2O)/R(Cl) \leq 0.1$ so that the calculated value of 5.5 is at least 55-fold larger than should be the case.

A final objection to the scheme as shown is that the frequency factor calculated for reaction 3 is almost equal to collision frequencies. While this is a weak objection in view of the uncertainty in collision diameters, it would nevertheless have been more comforting to find a smaller value.

It is possible to remove these objections by modifying the proposed scheme. There are indeed a number of mechanisms which are compatible with the experimental rate law A and do not fall afoul of the objections outlined above. To do the latter it is essential that the mechanism be a chain, not producing Cl atoms via

$$\frac{-d(N_2O)}{dt} \sim 2k_1(M)(Cl_2) \left[1 - \frac{4k_2^2}{k_3^2} \left(\frac{M}{N_2O} \right)^2 K_{eq}(Cl_2) \right].$$

This should be readily distinguishable from the rate law (A).

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³ Selected values of chemical thermodynamic properties, Circular

^{\$00,} National Bureau of Standards (1952). ⁴ Under conditions where $R(3) \ge 2R(2)$, the above scheme would give a rate law (using stationary state kinetics):

reaction 1. We shall outline two such schemes which deserve consideration.

The first of these arises from a reconsideration of Porter and Wright's⁵ work on the formation of ClO radicals by photolysis of Cl₂ and O₂ mixtures.

$$Cl_{2}+M\underset{2}{\overset{1}{\underset{2}{\longrightarrow}}}2Cl+M,$$

$$Cl+N_{2}O\underset{2}{\overset{3}{\longrightarrow}}N_{2}+ClO,$$

$$2ClO\underset{6}{\overset{4'}{\longrightarrow}}ClOO+Cl,$$

$$ClOO+M\underset{6}{\overset{5}{\underset{6}{\longrightarrow}}}Cl+O_{2}+M,$$

$$Cl+ClOO\underset{7}{\overset{7}{\longrightarrow}}Cl_{2}+O_{2}.$$

The replacement of reaction 4 by reaction 4' converts the scheme to a Cl-atom chain which no longer depends on the slow step 1. The heat of reaction 4' can be calculated to be, ${}^{6} \Delta H(4')=8-x$, where x is the bond dissociation energy of the Cl-O bond in the peroxy species ClO₂ (not to be confused with the isolatable species, O-Cl-O). If this bond energy is 8 kcal, which seems quite reasonable, then reaction 4' is thermoneutral and can be fast. In fact we should like to propose that the fast bimolecular disappearance of ClO observed by Porter and Wright takes place via the above sequence of reactions 4' and 7' rather than by the slow rearrangement of a dimeric species (ClO)₂ which they proposed.

At the elevated temperatures used in the N_2O experiments the equilibrium 51.6 is far to the right and it is to be anticipated that the lifetime of the peroxy ClO_2 (reaction 5) is very short. Reaction 7 is expected to be very fast but probably negligible compared to 5. If we

⁶ The value of D(Cl-OO) which we estimate at 8 kcal can be bracketed by the requirement that the equilibrium $2ClO \stackrel{4'}{=} ClO_2$ +Cl be nearly thermoneutral and that the equilibrium constant for $Cl \cdot O_2 \stackrel{5}{=} Cl + O_2$ be within an order of magnitude of 20 atmos (reference 8). The requirement of thermoneutrality comes from

The fact that Porter and Wright have shown that both reactions 4' and 7 must have activation energies not exceeding 1–2 kcal, i.e., they are both fast. With the value of 63 kcal for D(Cl-O) this gives $D(Cl-OO)=8\pm 2$ kcal. Starting with $\Delta H_{56}=T\Delta S_{66}$ $-RT \ln K_{56}$; using known thermal data for Cl and O₂ and assuming Cl-O-O to have 120° angle and r(Cl-O)=1.70 A; r(O-O)= 1.24 A, we calculate $S^{\circ}(ClOO)=61$ cal/mole-°K (compare with 63 cal/mole-°K for NOCl and 59.6 for symmetrical OClO). This gives $\Delta S_{56}=27.5$ cal/mole-°K and using $K_{5.6}=20$ atmos, we find $\Delta H_{5.6}=7.0\pm1$ kcal in good agreement. ⁷ The peroxy species ClO₂ was proposed by Porter and Wright to account for the Cl₂-catalyzed photo-oxidation of CO and also for the suppression of H₂+Cl₂ reaction in the presence of sufficient O₂. However, for some reason they suggested that the mechanism

⁷ The peroxy species ClO₂ was proposed by Porter and Wright to account for the Cl₂-catalyzed photo-oxidation of CO and also for the suppression of H_2+Cl_2 reaction in the presence of sufficient O₂. However, for some reason they suggested that the mechanism of ClO disappearance was via rearrangement of the "hot" molecule ClOOCI. Microscopic reversibility would then imply the production of ClO from excited Cl₂ plus O₂. The alternative to this, which is implied by the above mechanism is Cl+ClO₂ \rightarrow 2ClO which would compete with reaction 7. neglect reaction 7, this scheme yields for the stationary rate of disappearance of N_2O :

$$-d(N_2O)/dt = k_3(N_2O)(Cl)_{eq},$$
 (C)

which agrees with the empirical rate expression (A) and now has a sufficiently fast chain path for the reproduction of Cl atoms. The sole disturbing feature, and as already pointed out, a minor one, is the high value of the frequency factor of k_3 .

Two further reactions are worthy of consideration, and they are

$$ClO+N_2O \xrightarrow{8} N_2+O-Cl-O,$$

$$ClO+N_2O \xrightarrow{8'} N_2+Cl-O-O.$$

Reaction 8 is exothermic by 20 kcal which is the same value as for the proposed chain step 3. It might in principle be expected to have no higher an activation energy than 3 and thus participate in the over-all decomposition. The normal OCIO produced by reaction 8 could then disappear by either or both of the following:

$$O-Cl-O+Cl \rightarrow 2ClO,$$

$$O-Cl-O+ClO \rightarrow ClO+Cl-O-O$$

The isomerization reaction 10 has a heat of reaction, $\Delta H_{10} = (4-x)$ kcal and so is probably exothermic and may be expected to be reasonably fast under these conditions.⁸ Even stronger arguments can be made for the inclusion of reaction 8' in the chain since the destruction of Cl-O-O in step 5 is expected to be extremely rapid.⁹

The fastest chain would thus appear to be

$$Cl_{2}+M \xrightarrow{1}{2} 2Cl+M,$$

$$Cl+N_{2}O \xrightarrow{3} N_{2}+ClO,$$

$$ClO+N_{2}O \xrightarrow{8'} N_{2}+ClOO,$$

$$ClOO+M \xrightarrow{5} O_{2}+M+Cl,$$

where the rate would be given by:

$$-d(N_2O)/dt = 2k_3(N_2O)(Cl)_{eq}.$$
 (D)

⁸ If we assume that x=8 then $Cl-O_2$ is thermodynamically more stable than isomeric O-Cl-O by 4 kcal. One is justified in asking why Cl-OO is not a known species. The answer lies in its extreme reactivity, a consequence of the low bond-dissociation energy D(Cl-OO)=8 kcal, in contrast to the high bond-dissociation energy in O-Cl-O of 59 kcal.

tion energy in O-CI-O of 59 kcal. ⁹ The peroxy species CIOO seems to be the only way of accounting for the long chain lengths observed in the photolytic decompositions of OCIO and Cl₂O [see G. K. Rollefson and M. Burton, *Photochemistry and the Mechanisms of Chemical Reactions* (Prentice-Hall, Inc., Englewood Cliffs, 1939)] and the chain character of the explosions which both of these are known to undergo. It is likely that the chain explosion of ClO₂ is a degenerate branching chain set off by the isomerization reaction 10.

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⁶G. Porter and F. J. Wright, Discussions Faraday Soc. 14, 23 (1953).

The frequency factor of k_3 is thus reduced by a factor of 2 from that given by the previous expressions and is now less than the collision frequency.

While a similar scheme can be made for the Br_2 and I_2 catalyzed decompositions the arguments presented for the Cl_2 catalysis are not as compelling for these schemes¹⁰ and less is known about the hypohalite species BrO and IO. These species are certainly worthy of further investigation and may well play similar roles to ClO.

A final point is worthy of notice in connection with the peroxy ClOO species. If the bond dissociation energy of this species is indeed 8 kcal, then O_2 should be a fairly effective catalyst for the production of Cl atoms from Cl_2 at temperatures below 600°K. This would take place via the reaction:

$$O_2 + Cl_2 \xrightarrow{11} Cloo + Cl$$

whose enthalpy and probable activation energy is then 8 kcal less than the bond dissociation energy of Cl_2 . That this may be the case is already in evidence from the data of Porter and Wright⁴ to the effect that O_2 is about 46 times more effective in the recombination of Cl atoms than N_2 . The recombination presumably takes place through the intermediary ClOO via $Cl+O_2+M \rightarrow ClOO+M$.

Further support for the existence of Cl-O-O comes

from the work of Norrish¹¹ who followed the disappearance of ClO formed in the flash photolysis of normal OClO. At intensities high enough to photolyze all of the OClO presumably to O+ClO, they were able to reproduce the rate data of Porter and Wright on the rate of disappearance of the ClO species. However when they used excess OClO they found a decrease in the apparent second-order constant for the disappearance of ClO which became smaller with increasing excess of OClO. Such an effect is to be expected if the ClO disappears by reaction 4' followed with 5 regenerates Cl atoms, then followed by reaction 9 regenerating the ClO species, i.e.,

$$O-Cl-O+h\nu \rightarrow O+ClO,$$

$$O+O-Cl-O\rightarrow O_{2}^{*}+ClO,$$

$$2ClO \rightarrow Cl-O-O+Cl,$$

$$Cl-O-O+M \rightarrow Cl+O_{2}+M,$$

$$Cl+O-Cl-O \rightarrow 2ClO.$$

This would give the effect of a "slower" rate for 4' if reaction 9 is reasonably fast.¹²

¹¹ Lipscomb, Norrish, and Thrush, Proc. Roy. Soc. (London) A233, 455 (1956).

¹⁰ Thus the ratios $R(N_2O)/R(X)$ are in the range of 0.8 to 0.1 for X=Br, I, which are not too much above the value of 0.1.

¹² Norrish *et al.* show that the alternative explanation, the formation of a labile oxide Cl_2O_3 in rapid equilibrium with ClO+OClO, would require a rather large equilibrium constant requiring so high a heat of dissociation (15 kcal) as to cause impossibly slow dissociation of Cl_2O_3 in the times observed.