THERMAL DECOMPOSITION OF OZONE

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As was shown in [1], the thermal decomposition of ozone follows the following mechanism rather accurately:

\[ \frac{k_1}{k_{-1}} O_3 + M = O_2 + O + M \quad (1, -1) \]

\[ \frac{k_2}{k_{-2}} 0 + O_3 = O_2 + O_2 \quad (2) \]

The process

\[ O_3 + O_2 = 3O_2 \quad (3) \]

introduced by Glissman and Schumacher [2], while playing some role in this reaction, does so only at low temperatures and high concentrations of ozone.

On the basis of the value of the constant \( k_1 \) that they measured at one temperature (100°) and the data of [2], Benson and Axworthy obtained the formula \( k_1 = 4.61 \cdot 10^{15} e^{-24,000/RT} \text{ cm}^3 \cdot \text{ mole}^{-1} \cdot \text{ sec}^{-1} \) for the temperature interval 70-110° and \( M = O_2 \). Somewhat later [3], a formula close to this was obtained, \( k_1 = 8.10^{15} e^{-24,300/RT} \text{ cm}^3 \cdot \text{ mole}^{-1} \cdot \text{ sec}^{-1} \) (also for \( M = O_2 \)) for the interval 115-130°. In [4], the constant \( k_1 \) was measured in a shock tube for \( M = N_2 \) within the temperature interval 416-590° and for \( M = Ar \) within the interval 496-637°. For \( M = N_2 \), from the data of [4], the following formula can be obtained: \( k_1 = 2.44 \cdot 10^{14} e^{-21,300/RT} \text{ cm}^3 \cdot \text{ mole}^{-1} \cdot \text{ sec}^{-1} \) for the interval 416-590°.

Despite a certain difference of the three formulas cited above, for the constant \( k_1 \), the latter can be represented with a good degree of accuracy by an Arrhenius formula within the entire range of temperatures studies. Thus, for \( M = O_2 \), assuming the efficiency of oxygen to be equal to 0.44 of the efficiency of ozone [1, 5], and taking the average value of the efficiency of nitrogen with respect to the efficiency of oxygen, measured in [1, 5-8], as 0.72, we obtain

\[ k_{O_3} = 7.8 \cdot 10^{14} e^{-23500/RT} \text{ cm}^3 \cdot M^{-1} \cdot \text{ sec}^{-1} \]

(t = 70-590°). Let us mention that for the same temperature interval and \( M = N_2 \), on the basis of the data of [1] and [4], Jones and Davidson obtained the following formula [4]:

\[ k_{N_2} = 5.8 \cdot 10^{14} e^{-22150/RT} \text{ cm}^3 \cdot M^{-1} \cdot \text{ sec}^{-1} \]

If the data of various authors [1-4], pertaining to the determination of the constant \( k_1 \), can be considered to be practically coinciding, the rate constants of the other two processes, entering into the mechanism of the decomposition of ozone, \( k_{-1} \) and \( k_2 \), measured by various authors, frequently differ sharply. As for the constant \( k_{-1} \), here an especially great dispersion (within the limits of one order of magnitude) is observed in the case of the values measured close to room temperature [6, 9-13].

The causes of this dispersion were considered in [13, 14]. The dispersion of the values of \( k_{-1} \), correlated from the measured constant \( k_1 \) and the constant of the equilibrium \( O_3 = O_2 + O(K) \), can be partially ascribed to the fact that various authors used different data on the insufficiently accurately known equilibrium constant. However, it should be indicated that despite the dispersion of \( k_{-1} \), the available data leave no doubt that this constant, like other rate constants of third order recombination processes, decreases

* We have in mind the data pertaining to \( M = O_2 \).
with increasing temperature. In representing the constant \( k_1 \) by an Arrhenius formula, various authors have obtained the following values for the activation energy: \( E_1 = -0.7 \) \([6]\), \(-0.89 \) \([15]\) kcal/mole for \( M = O_2 \) and \( E = -1.9 \) \([16]\), \(-1.8 \pm 0.4 \) \([17]\), \(-1.7 \pm 0.3 \) \([4]\) for \( M = Ar \). Only in \([3]\) is the value \( E_1 = +0.3 \) kcal/mole cited. Since this number was obtained according to four points within a narrow range 115-130\(^\circ\), with a dispersion that permitted the authors in a preliminary communication to assume \( E_1 = -0.4 \) kcal/mole, the result obtained evidently should be neglected.

A substantial dispersion in individual values and the corresponding formulas is also observed in the case of the constant \( k_2 \). Thus, for 50\(^\circ\), for the data of various authors, the following values of \( k_2 \) are obtained: \( 1.8 \cdot 10^9 \) \([18]\), \( 4.5 \cdot 10^9 \) \([3]\), \( 1.5 \cdot 10^9 \) \([17]\) and \( 1.0 \cdot 10^9 \) \([15]\) cm\(^3\)·mole\(^{-1}\)·sec\(^{-1}\), with a comparatively small dispersion of the values of the activation energy \( E_2 \): \( 1 \pm 1 \) \([1]\), \( 3.2 \) \([3]\), \( 4.5 \) \([17]\) and \( 5.7 \) \([15]\) kcal per mole. In all the enumerated studies, with the exception of \([17]\), the constant \( k_2 \) was found from the measured ratio \( k_2/k_1 \). Therefore it is natural that the dispersion of the values of \( k_1 \) was reflected in the dispersion of \( k_2 \). In view of the aforementioned, it was interesting to measure the constants \( k_1 \) and \( k_2 \) in order to determine them more accurately and reliably.

**EXPERIMENTAL**

In our experiments the reaction vessel represented a glass tube with a total length of 110 cm and inner diameter 9 mm, coiled into a spiral. The diameter of each turn was equal to 3 cm. The tube was placed in an electric furnace with uniform temperature distribution along its length. The experiments were conducted in a stream of gas at temperatures from 136 to 226\(^\circ\) and atmospheric pressure. The linear velocity of the gas was 3.7-4.5 cm/sec.

Electrolytic oxygen, after entering the reaction vessel from the cylinder, was passed through an ozonator. The ozone content was no more than 2.6\%. At such an ozone content in oxygen, the heating of the gas as a result of the exothermic reaction \( O_3 = \frac{3}{2}O_2 + 35 \text{ kcal/mole} \) comprised < 1\(^\circ\), which was established by special measurements. The ozone concentration was measured by titration (with sodium hyposulfite) of the iodine formed during passage of the gas through a potassium iodide solution (50 g of KI per liter).

It is not difficult to show that under the conditions of our experiments, despite the small diameter of the reaction vessel, the heterogeneous destruction of oxygen atoms, the rate of which is determined by the rate of diffusion of atoms to the walls, occurs several hundred times more slowly than the recombination volume process \((-1)\). Therefore it may be assumed that under these conditions, the reaction mechanism can be represented with a sufficient degree of accuracy by processes expressed by equations \((1, -1)\) and \((2)\). Assuming the applicability of the conclusion of a stationary state of the oxygen atoms, for the rate of decomposition of ozone we obtain the following expression

\[
\frac{d[O_3]}{dt} = \frac{2k_1k_2[M][O_3]^2}{k_1[M][O_2] + k_2[O_3]}
\]

Let us show that in this case the concentration of oxygen atoms can be considered stationary with a great degree of accuracy. Actually, integrating the equation

\[
\frac{d[O]}{dt} k_1[M][O_2] - (k_{-1}[M][O_2] + k_2[O_2])[O]
\]

in the initial period of the reaction, when the ozone concentration still differs little from the initial concentration \([O_3]_0\), we will have

\[
[O] = \frac{[O]_{stat}}{1 - e^{-t/\tau}}
\]

where \([O]_{stat}\) is the stationary concentration of O atoms, i.e., the concentration corresponding to the condition of the stationary state \(d[O]/dt = 0\), and

\[
\tau = \frac{1}{k_{-1}[M][O_2] + k_2[O_2]_0}
\]

is the time of establishment of the stationary concentration. Noting that

\[
\tau < \frac{1}{k_{-1}[M][O_2]}
\]