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PHYSICAL CHEMISTRY

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Abstract

Full Text

PHYSICAL CHEMISTRY

R. F. Vasil' ev and A. A. Vichutinskii

ON THE NATURE OF THE RELATION BETWEEN CHEMILUMINESCENCE AND OXIDATION BY MOLECULAR OXYGEN

(Presented by Academician V. N. Kondrat' ev, 10 VII 1961)

Chemiluminescence has most often been observed in reactions of oxidation by molecular oxygen or by other substances that readily liberate molecular oxygen⁽¹⁾. The special connection between chemiluminescence and oxidation was first established by Robert Boyle as early as the seventeenth century. In a recent monograph by C. Reid⁽²⁾ the existence of this connection is also noted, and it is emphasized that its nature remains uninvestigated and unclear up to the present time—all the more so since oxygen is well known as a quencher of photoluminescence. Very recently, with the aid of highly sensitive photoelectric apparatus, chemiluminescence has been detected in many chemical reactions of various classes^(3,4). It has been shown that in reactions proceeding with the participation of free radicals, excitation of the emission occurs in elementary acts of radical recombination⁽⁴⁾. It turned out that in these reactions as well, introducing oxygen into the system invariably leads to an intensification of chemiluminescence, i.e., the special role of oxygen is likewise manifested.

In the present work it has been established that, in radical reactions, the intensification of chemiluminescence upon introducing oxygen into the system is chemical in nature. It is associated with the appearance of peroxide radicals in the reaction and with high light yields upon recombination of peroxide radicals.

We studied the kinetics of chemiluminescence in the reaction of the thermal decomposition of α, α' -azobisisobutyronitrile (AIBN) in hydrocarbon solutions. The solution filled a glass thermostated vessel placed in front of a photomultiplier (the layout of the apparatus is described in detail in⁽⁵⁾). The main experiments were carried out at 60°.

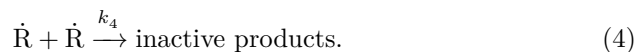
Decomposition of AIBN in the presence of a hydrocarbon leads to the formation of hydrocarbon radicals in the system:



The rate w_i of formation of radicals during decomposition of this substance

(the rate of initiation) is, at 60°, equal to $1.2 \cdot 10^{-5}$ [AIBN] mol/l · sec ⁽⁶⁾ and is practically constant in time, since at this temperature AIBN decomposes by 2% in 40 min.

Chemiluminescence in reactions of thermal decomposition arises upon recombination of radicals:



Its intensity is equal to

$$I_4 = f_4 k_4 (\dot{R})^2$$

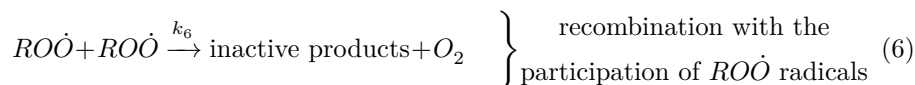
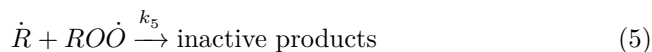
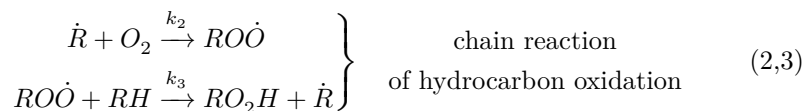
or, since in the steady-state regime the rate of termination is equal to the rate of initiation:

$$I_4 = f_4 w_i,$$

where f_4 is the light yield, or the probability of photon emission upon recombination*.

* The magnitude of f for this type of reaction is of the order of 10^{-8} – 10^{-10} ⁽³⁾.

Upon the introduction of oxygen, a system is formed in which initiated oxidation of the hydrocarbon proceeds, and the extremely simple reaction scheme given above is supplemented by new processes ⁽⁷⁾:



It is known ⁽⁸⁾ that the rate constant k_2 is so large that even at very low concentrations of O_2 practically all \dot{R} radicals are replaced by RO_2 , and the oxidation rate w_{O_2} ceases to depend on the oxygen concentration:

$$w_{O_2} = -\frac{d[O_2]}{dt} = \frac{k_3}{\sqrt{k_6}} \sqrt{w_i} [RH] + \frac{1}{2} w_i. \quad (7)$$

In this case one may neglect termination reactions (4) and (5) and assume that chemiluminescence is excited only in reaction (6)

$$I_6 = f_6 k_6 [RO\dot{O}]^2 = f_6 w_i,$$

where I_6 and f_6 are the intensity and yield of chemiluminescence upon recombination of peroxy radicals. Comparison of the expressions for I_4 and I_6 shows that

$$\frac{I_6}{I_4} = \frac{f_6}{f_4},$$

i.e., if $f_6 \neq f_4$, then the glow intensity in the absence and in the presence of oxygen must be different.

If this conclusion—and hence the initial premise concerning the mechanism of the effect of O_2 on chemiluminescence—is correct, then upon gradual decrease in the concentration of dissolved oxygen we should observe a change in the glow intensity associated with replacement of $RO\dot{O}$ radicals by \dot{R} radicals. This effect was observed by us for several hydrocarbons. In these experiments the solution was saturated with air or oxygen; then the reaction vessel was closed with a ground-glass stopper so that no gas bubbles remained in it, and consumption of dissolved oxygen began in it. After a prolonged (tens of minutes) interval of constant intensity, when the reaction rate and the concentration of $RO\dot{O}$ radicals do not depend on the oxygen concentration and are constant, a rapid drop in intensity occurred.

In Fig. 1, as an example, curves are shown for three hydrocarbons for the transition from the stationary state in the presence of O_2 , when only $RO\dot{O}$ radicals are present in the system, to the stationary state in the absence of O_2 , when only \dot{R} radicals recombine. In all cases f_6 proves to be greater than f_4 . This can be explained by the fact that, upon recombination of $RO\dot{O}$ radicals, strongly luminescent oxygen-containing products are formed, which convert the reaction energy into radiation energy with greater efficiency than do hydrocarbons—the products of recombination of \dot{R} radicals⁽⁹⁾.

Since replacement of $RO\dot{O}$ radicals by \dot{R} occurs at low concentrations of O_2 , it may be assumed that the moment of the drop corresponds to practically complete consumption of the oxygen. From scheme (1)–(6) it is not difficult to obtain the following equation:

$$\frac{1}{t} = \frac{w_{O_2}}{[O_2]_0} = \alpha [RH] + \beta, \quad \alpha = \frac{k_3}{\sqrt{k_6}} \frac{\sqrt{w_i}}{[O_2]_0}, \quad \beta = \frac{w_i}{2[O_2]_0}, \quad (8)$$

where t is the duration of the reaction, i.e., the time from the beginning of O_2 consumption to the decay of the luminescence.

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

By measuring the reaction time at different hydrocarbon concentrations, from equation (8) one can find the parameters α and β and determine the ratio $k_3/\sqrt{k_6}$.

$$\frac{k_3}{\sqrt{k_6}} = \frac{\alpha}{2\beta} \sqrt{\omega_i}. \quad (9)$$

It is seen from Fig. 2 that equation (8) is well satisfied for the two hydrocarbons investigated by us—ethylbenzene and cumene. The slope

Fig. 1. Kinetics of the decay of chemiluminescence intensity caused by replacement of peroxy radicals by hydrocarbon radicals in the oxidation reactions of toluene (1), ethylbenzene (2), and decalin (3), initiated by AIBN. Hydrocarbon concentrations 2 vol. %, $[AIBN] = 6.1 \cdot 10^{-2}$ mol/l, temperature 63° , solvent—benzene

Fig. 2. Dependence of the reciprocal reaction time on the hydrocarbon concentration in cumene in the oxidation reactions of ethylbenzene (1) and cumene (2), initiated by AIBN ($6.1 \cdot 10^{-2}$ mol/l) at 60° . The reaction mixture was saturated with oxygen by passing dried air through it

of the straight lines depends on the reactivity of the hydrocarbons and must be proportional to the value $k_3/\sqrt{k_6}$. Indeed, the slopes of straight lines 1 and 2 differ by a factor of 3.0, which is close to the values

$(k_3/\sqrt{k_6})_{\text{cum}} : (k_3/\sqrt{k_6})_{\text{ethyl}} = 4.6-5.5$, calculated from data of other authors (6,10,11).

The ratio $k_3/\sqrt{k_6}$ for ethylbenzene, found from formula (9), is $4.6 \cdot 10^{-4} \text{ l}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{sec}^{-1/2}$, which differs little from the value $5.7 \cdot 10^{-4} \text{ l}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{sec}^{-1/2}$, obtained at 60° by Z. G. Kozlova, V. F. Tsepalov, and V. Ya. Shlyapintokh (10).

The reaction time t when the solution is saturated with air (20.9% O_2) is 20.4% of the time corresponding to saturation with 100% O_2 , i.e., in accordance with formula (8), t is proportional to $[O_2]_0$.

It follows from Fig. 2 that, in accordance with formula (8), the segment β cut off on the ordinate axis is practically independent of the kind of hydrocarbon.

Thus, equation (8) completely describes the results obtained and leads to correct values of the quantity calculated from it.

the value $k_3/\sqrt{k_6}$. This is quantitative evidence for the hypothesis advanced above concerning the chemical nature of the stimulating action of oxygen on chemiluminescence in radical reactions.

It is evident that measurements of the kinetics of the chemiluminescence accompanying the oxidation of hydrocarbons in a closed system can be used as a method for determining the ratios of the constants of elementary steps.

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CITED LITERATURE

1. B. Ya. Sveshnikov, *Priroda*, No. 2, 15 (1941).
2. S. Reid, *Excited Electronic States in Chemistry and Biology*, Moscow, 1960.
3. R. F. Vasil' ev, O. N. Karpukhin, V. Ya. Shlyapintokh, DAN, **125**, No. 1, 106 (1959).
4. R. F. Vasil' ev, A. A. Vinutinskii, O. N. Karpukhin, L. M. Postnikov, V. Ya. Shlyapintokh, *Transactions on Chemistry and Chemical Technology*, Gorky, No. 1, 44 (1961).
5. R. F. Vasil' ev, O. N. Karpukhin, V. Ya. Shlyapintokh, ZhFKh, **35**, No. 2, 461 (1961).
6. G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).
7. D. G. Knorre, Z. K. Maizus, L. K. Obukhova, N. M. Emanuel' , *Uspekhi Khimii*, **26**, No. 4, 416 (1957).
8. Ch. Walling, *Free Radicals in Solution*, IL, 1960.
9. R. F. Vasil' ev, A. A. Vinutinskii, O. N. Karpukhin, V. Ya. Shlyapintokh, *Proceedings of the XIII Conference on Spectroscopy*, IL, 1960.
10. Z. G. Kozlova, V. F. Tsepalov, V. Ya. Shlyapintokh, *Transactions on Chemistry and Chemical Technology*, Gorky, No. 1, 95 (1961).
11. H. W. Melville, S. Richards, *J. Chem. Soc.*, **1954**, 944.

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