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R. F. Vasil' ev

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Figure 1.

Figure 1: Figure 1.

Abstract

Full Text

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R. F. Vasil' ev

Kinetics of Chemiluminescence and the Study of Reactions of Liquid-Phase Oxidation of Hydrocarbons

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1. Recently, chemiluminescence has been discovered in many slow chemical reactions, including reactions of liquid-phase oxidation of hydrocarbons ([1,2]). It has been shown that the introduction of components that react with the radicals of the system and thus change their composition leads to a change in the intensity of luminescence ([3]). Obviously, the reverse process as well—the disappearance of one of the components of the reacting mixture during the course of the reaction—will lead to a change in the composition of the radicals and to a change in the intensity of chemiluminescence.

Fig. 1. 1 $-w_i = 1.5 \cdot 10^{-7}$ mol $\cdot$ l^{-1} $\cdot$ sec^{-1}, [RH] = 5.8 mol $\cdot$ l^{-1}; 2 $- w_i = 1.5 \cdot 10^{-7}$, [RH] = 0.39; 3 $-w_i = 1.84 \cdot 10^{-6}$, [RH] = 5.8; 4 $-w_i = 1.5 \cdot 10^{-6}$, [RH] = 0.39

Since the oxidation of hydrocarbons by dissolved oxygen and its consumption in the course of this reaction lead to a weakening of the luminescence caused by the replacement of peroxide radicals $RO_2^\bullet$ by hydrocarbon radicals $R^\bullet$.

Figure 1 presents the kinetics of the weakening of chemiluminescence in the oxidation reaction of ethylbenzene at 60°. To average the noise, each

the experiment was repeated 2-3 times. Segment *a* of curve 4 illustrates the inertia of the recording system (the time required to reach 100% intensity).

O. N. Karpukhin and V. Ya. Shlyapintokh showed that introducing the inhibitor InH into the oxidizing mixture and replacing the active radicals $RO_2^\bullet$ by the low-active radicals $In^\bullet$ weakens the luminescence ([3]). However, as the inhibitor is consumed, the initial intensity is restored.

Fig. 2. Inhibitors: 1, 2, 3—ionol (2,6-di-tert-butyl-4-methylphenol); 4—*o*-cyclopentenyl-*p*-cresol. Initial inhibitor concentrations: 1—$0.23 \cdot 10^{-3}$; 2—$0.70 \cdot$

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

10^{-3}; 3—$1.4 \cdot 10^{-3}$; 4—$5.8 \cdot 10^{-3}$ mol/l.

Figure 2 presents the kinetics of the change in the intensity of chemiluminescence accompanying the initiated oxidation of ethylbenzene (0.78 mol/l) in chlorobenzene solution in the presence of inhibitors. Temperature 60°. Initiation rate $0.75 \cdot 10^{-6}$ mol $\cdot$ $l^{-1} \cdot sec^{-1}$.

Figure 3 presents the kinetics of the change in the intensity of chemiluminescence accompanying the initiated oxidation of ethylbenzene in benzene solution in the presence of ionol. Temperature 60°. Initiation rate $3.0 \cdot 10^{-6}$ mol $\cdot$ $l^{-1} \cdot sec^{-1}$.

Fig. 3. Ethylbenzene concentration: 1 and 3—0.78 mol $\cdot$ l^{-1}, 2—6.8; ionol concentration $3.7 \cdot 10^{-3}$ mol $\cdot$ l^{-1}. 1 and 2 at constant saturation of the reaction mixture with oxygen; 3—the mixture was kept for the first 45 min in the absence of oxygen.

Common to the curves shown in Figs. 1, 2, and 3 is a more or less abrupt change in intensity, a sharp transition from one stationary regime to another, each of which corresponds (at constant initiation rate ω_i) to a constant concentration of radicals of one or another type ($RO_2^\bullet$ or $R^\bullet$, $In^\bullet$ or $RO_2^\bullet$).

2. The intensity of chemiluminescence is ultimately determined by the concentrations of reagents, the rate constants of the elementary steps, and the luminescence yield. The kinetics of its change can in principle be calculated from the corresponding reaction scheme. However, even without carrying out detailed calculations, one can arrive at certain conclusions about the type of information provided in the cases mentioned by the kinetics of chemiluminescence.

Let us consider any reaction in which the change in the type of radicals and the consumption of component A occur in one and the same elementary step:

$$\mathrm{r_i^\bullet + A \xrightarrow{k_a} r_j^{\bullet\prime} + (A'),}$$

and chemiluminescence is excited in reactions of quadratic radical termination: in one of the stationary states (B), in the process

$$\mathrm{r^\bullet + r^\bullet \xrightarrow{k_b} inactive\ products}$$

in the other (C)—in the process

$$r^\bullet + r'^\bullet \xrightarrow{k_c} \text{inactive products,}$$

where k_b and k_c are rate constants, and $r^\bullet$ and $r'^\bullet$ are radicals (for example, in the case of introducing oxygen $r^\bullet = R^\bullet$, $r' = RO_2^\bullet$, $A = O_2$; in the case of introducing the inhibitor InH, $r^\bullet = RO_2^\bullet$, $r' = In^\bullet$, $A = InH$, $A' = RO_2H$). The equation for the rate of consumption of A is written in the form

$$-\frac{d[A]}{dt} = k_a[r^\bullet][A]. \qquad (1)$$

In the stationary regime (B), the concentration of radicals $r^\bullet$ is

$$[r^\bullet] = \sqrt{\frac{w_i}{k_b}} = \text{const},$$

where w_i is the constant rate of initiation. In the region of transition from one regime to another, $[r^\bullet]$ decreases and amounts to a fraction ρ of the value $\sqrt{w_i/k_b}$. Denoting $[r^\bullet] = \sqrt{w_i/k_b}\,\rho$, we write equation (1) in the form

$$-\frac{d[A]}{dt} = \frac{k_a}{\sqrt{k_b}}\sqrt{w_i}\,\rho[A]$$

or

$$-\frac{d[A]}{d\left(\frac{k_a}{\sqrt{k_b}}\sqrt{w_i}\,t\right)} = \rho[A]. \qquad (2)$$

It follows from equation (2) that, in this approximation, for different substances A (i.e., different k_a and k_b) and different initiation rates w_i, the form of the kinetic curves for consumption of A will be one and the same, if the same reaction mechanism is operating. Only the scale along the time axis will change, and the transformation coefficient will be equal to the ratio of the quantities $k_a\sqrt{w_i}/\sqrt{k_b}$. Since it is precisely the concentration of substance A that determines the concentrations of radicals and the intensity of emission, the kinetic curve of chemiluminescence will change on the same scale. For example, for more effective inhibitors the increase in emission intensity should be steeper than for less effective ones.

In Fig. 2 it is clearly seen that the chemiluminescence intensity curves for two inhibitors, 2,6-di-tert-butyl-4-methylphenol (ionol) and *o*-cyclopentenyl-*p*-cresol (synthesized by N. I. Shuikin and E. A. Viktorova), differ in steepness by a factor of 10–12, in agreement with S. I. Polina' s data that the first inhibitor is 10–15 times more effective than the second (at 90°). The enhancement of chemiluminescence begins the earlier, the lower the initial concentration and effectiveness of the inhibitor and the higher the initiation rate.

The form of the curve of intensity increase also depends on the initiation rate: in accordance with equation (2), the maximum slope of curves 1-3 (Fig. 3) is twice as great as the slope of curves 1-3 (Fig. 2), taken at an initiation rate 4 times smaller (see also Fig. 1).

3. If a mixture consisting of a hydrocarbon, an initiator, and an inhibitor is kept in the absence of oxygen for the time required (under continuous oxygen supply) for almost complete consumption of the inhibitor, this only shifts the kinetic curve of the emission intensity (curve 3 in Fig. 3). This result resolves the very important question of which radical—peroxide or hydrocarbon—the inhibitor reacts with. It is obvious that, in this case, in the absence of oxygen the inhibitor is not consumed, i.e., ionol reacts only with peroxide radicals.
4. If the reaction scheme is known, then one can calculate the kinetics of chemiluminescence and find ratios of the rate constants. We calculated, on an electronic computer, the decay curves of chemiluminescence caused by oxygen consumption (Fig. 1) according to the well-founded scheme of hydrocarbon oxidation (see, for example, (5)).

Chain initiation (appearance of radicals $R^\bullet$) at the rate w_i

$$\cdots \to R^\bullet \tag{I}$$

$$\text{Chain} \begin{cases} R^\bullet + O_2 \xrightarrow{k_2} RO_2^\bullet, \\ RO_2^\bullet + RH \xrightarrow{k_3} R^\bullet + RO_2H \end{cases} \tag{II–III}$$

$$\text{Chain termination} \quad \begin{cases} R^\bullet + R^\bullet & \to \text{inactive products}, \\ R^\bullet + RO_2^\bullet & \to \text{inactive products}, \\ RO_2^\bullet + RO_2^\bullet & \to \text{inactive products} + O_2. \end{cases} \tag{IV–VI}$$

(k_i are the rate constants of the i-th elementary step).

Although in the experiments the concentration of ethylbenzene and the initiation rate were varied by a factor of 12-15 (Fig. 1), the ratio $k_2/\sqrt{k_4}$, calculated from comparison of the theoretical and experimental curves, remained constant within ±30%, and its mean value proved to be $2.7 \cdot 10^4\ l^{-1/2} \cdot mol^{-1/2} \cdot sec^{-1/2}$, i.e., of the same order as for tetralin—a hydrocarbon for which this ratio was estimated by another method (from oxygen absorption) (6).* For methyl oleate a value of $3 \cdot 10^2\ l^{-1/2} \cdot mol^{-1/2} \cdot sec^{-1/2}$ was obtained, close to the literature value $5 \cdot 10^2\ l^{-1/2} \cdot mol^{-1/2} \cdot sec^{-1/2}$ (9).

5. Thus, changes in the kinetics of chemiluminescence in oxidation reactions are a rapid means of obtaining valuable information on the kinetics and mechanism of the oxidation reaction, on the values of ratios of elementary constants, on the relative activity of inhibitors, and on the mechanism of their action. In addition, as proposed in (^{7}), it is possible to measure the ratio $k_3/\sqrt{k_6}$, the concentration of dissolved oxygen, and the rate of its change, and to obtain data on the mechanism of the stages of initiation and recombination of peroxide radicals. In this case, the only quantitative characteristic of the system that must be known before the experiment is the initiation rate (or the solubility of oxygen). The limits of applicability of the chemiluminescence method can be expanded by "sensitizing" the chemiluminescence with additives of strongly luminescent substances that increase the intensity of the glow (^{8}).

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Institute of Chemical Physics
Academy of Sciences of the USSR

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* Experimental determination of the ratio $k_2/\sqrt{k_4}$ presents considerable difficulties, which are connected with the need to measure the oxidation rate at very low oxygen concentrations. Therefore this ratio has been measured only for a few hydrocarbons (tetralin and several olefins).