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ON THE HIGH REACTIVITY OF PEROXIDE RADICALS IN AN OXIDATION-REDUCTION REACTION

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Salts of metals of variable valence are widely used as catalysts for the oxidation of various organic substances. It is known that the rate of an oxidation reaction depends directly on the concentration of active centers—peroxide radicals $RO_2^{\cdot}$. Owing to the fact that the peroxide radical possesses oxidizing properties, under certain conditions its interaction with a salt of a metal in the lower valence state becomes possible. In this process the transfer of one electron from Me^{n+} to the $RO_2^{\cdot}$ radical leads to the destruction of the free valence (termination of the oxidation chain). The macrokinetic consequence of this elementary act is a decrease in the rate of oxidation ([1,2]). In some cases the presence of a manganese salt in the reaction zone may lead to complete cessation of the chain oxidation process that has developed ([3]).

At present this class of reactions—the interaction of salts of transition metals with radicals—has scarcely been studied quantitatively. In our work ([4]) it was shown that the rate constant of the reaction between a complex salt of divalent manganese and the $RO_2^{\cdot}$ radical in an oxidizing hydrocarbon medium is 10^5 l/mole · sec. For more precise quantitative studies, the chemiluminescence method ([5]) was used in the present work. The interaction of peroxide radicals with manganese stearate was studied in the chemiluminescence apparatus described in ([6]).

It is known that oxidation reactions of hydrocarbons are accompanied by luminescence, the source of which is the process of quadratic recombination of peroxide radicals:

$$RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_6} \text{molecular products} + h\,.$$

If peroxide radicals are generated in the reaction at a constant rate w_i, then $w_i = k_6[RO_2^{\cdot}]^2 = \text{const}$, and the chemiluminescence intensity will remain constant. When an agent reacting with $RO_2^{\cdot}$ (an inhibitor) is introduced into such a

reaction system, the rate of quadratic recombination decreases and, correspondingly, the chemiluminescence intensity decreases (7).

Figure 1 shows a typical chemiluminescence diagram. The reaction was carried out in a glass thermostated reactor with oxygen bubbling in the presence of an activator (dibromoanthracene) at a concentration of 1 mg/ml. Azobisisobutyronitrile was used as the source of radicals, and chlorobenzene served as the inert solvent. As can be seen from Fig. 1, the steady-state regime characterizing the decomposition of the initiator in chlorobenzene gives a constant chemiluminescence intensity. After the introduction of manganese stearate (shown in the figure by an arrow), the luminescence intensity rapidly falls, and then, as the manganese passes into the trivalent form, reaches its former value. In this experiment the temperature was 80°, $[MnSt_2] = 1.3 \cdot 10^{-5}$ mole/l, $w_i = 5 \cdot 10^{-8}$ mole/l · sec.

Consider the reactions occurring in the system under study: an inert solvent, initiator Y, and the transition-metal salt $MnSt_2$.

1. $Y \xrightarrow{w_i} RO_2^{\bullet}$.
2. $RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{k_6} h\nu$, quadratic termination.
3. $RO_2^{\bullet} + MnSt_2 \xrightarrow{k_7}$ $MnOHSt_2$+ molecular products.

The kinetics of these reactions is described by the system of differential equations

$$d[RO_2^{\bullet}]/dt = w_i - k_7[RO_2^{\bullet}][Mn] - k_6[RO_2^{\bullet}]^2; \tag{1}$$

$$d[Mn]/dt = -k_7[RO_2^{\bullet}][Mn]. \tag{2}$$

As shown in work (7), the concentration of radicals is proportional to the square root of the luminescence intensity,

$$[RO_2^{\bullet}] = [RO_2^{\bullet}]_0\sqrt{I/I_0} = \sqrt{w_i/k_6}\sqrt{I/I_0},$$

where $[RO_2^{\bullet}]$, I, $[RO_2^{\bullet}]_0$, and I_0 are, respectively, the radical concentrations and chemiluminescence intensities at the time of initiation and under the initial conditions, i.e., before the introduction of the manganese salt. Substituting this expression into (1) and using the steady-state principle, we obtain

$$\sqrt{w_i/k_6}\, d(\sqrt{I/I_0})/dt = w_i - k_7\sqrt{w_i/k_6}\sqrt{I/I_0}\,[Mn] - k_6\frac{w_i}{k_6}\frac{I}{I_0} = 0,$$

$$[\mathrm{Mn}] = \frac{w_i - k_6(w_i/k_6)(I/I_0)}{k_7\sqrt{w_i/k_6}\sqrt{I/I_0}} = \frac{\sqrt{w_i k_6}}{k_7}\left(\sqrt{\frac{I_0}{I}} - \sqrt{\frac{I}{I_0}}\right) = \frac{\sqrt{w_i k_6}}{k_7}\frac{I_0 - I}{\sqrt{I_0 I}}. \tag{3}$$

Let $\sqrt{I/I_0} = x$, and substitute the values found for $[\mathrm{RO}_2^\bullet]$ and [Mn] into equation (2):

$$dx\left[\frac{1}{x^2(1-x^2)} + \frac{1}{1-x^2}\right] = k_7\sqrt{\frac{w_i}{k_6}}\,dt. \tag{4}$$

Integrating this equation, we obtain

$$\ln\left[\frac{1+x}{1-x}\right] - \frac{1}{x} = k_7\sqrt{\frac{w_i}{k_6}}\,t + C. \tag{4a}$$

In the coordinates of this equation, the dependence of the chemiluminescence intensity on time should be linear, and from the tangent of the angle of inclination, for a given value of w_i, one can obtain the ratio $k_7/\sqrt{k_6}$.

In Fig. 1, straight line 1 represents the dependence

$$\lg\frac{1+\sqrt{I/I_0}}{1-\sqrt{I/I_0}} - 0.43\sqrt{\frac{I_0}{I}}$$

on time; the value of $k_7/\sqrt{k_6}$ calculated from this graph is 76.0 $(\mathrm{l/mol\cdot sec})^{1/2}$. The mean value of the ratio $k_7/\sqrt{k_6}$, obtained in an analogous manner from the experimental data of 6 experiments, is 75.0 $(\mathrm{l/mol\cdot sec})^{1/2}$.

From the chemiluminescence diagram, at each moment one can calculate the ratio $(I_0-I)/\sqrt{II_0}$, which, according to equation (3), is proportional to the concentration of $MnSt_2$. In Fig. 2, curve 1 describes the dependence of $(I_0-I)/\sqrt{II_0}$ on time, i.e., it depicts the change in [Mn] during the reaction. The semilogarithmic anamorphosis of this curve (straight line 2) shows that, beginning at a certain depth of conversion, the change in salt concentration follows a first-order reaction. This is understandable if one takes into account that, at a chemiluminescence intensity equal to half the initial value, the radical concentration is 70% of the initial one.

the value $[\mathrm{RO}_2^\bullet]_0$. As the manganese salt is consumed, $[\mathrm{RO}_2^\bullet]$ rises to the initial value. Thus, over a long portion of the reaction the concentration of radicals changes by 30%, i.e., to a certain approximation it may be considered constant. Then

Fig. 1. 1 –kinetic curve of the change in chemiluminescence intensity in the interaction of $\mathrm{RO}_2^\bullet$ and $MnSt_2$ (the arrow indicates the moment of introduction

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

of a manganese stearate solution into the reaction); 2 –anamorphosis of curve 1 in the coordinates of equation (4a)

Fig. 2. 1 –kinetic curve of the change in the concentration of the manganese salt; 2 –semilogarithmic anamorphosis of curve 1

$$-\frac{d[\mathrm{Mn}]}{dt} \simeq k_7[\mathrm{RO_2}]_0[\mathrm{Mn}] = k_7\frac{\sqrt{w_i}}{\sqrt{k_6}}[\mathrm{Mn}] \tag{10}$$

The value of $k_7/\sqrt{k_6}$, calculated from the slope of the semilogarithmic anamorphosis, is 56.

Finally, the current concentration [Mn] can be calculated graphically. In Fig. 1 the area under the chemiluminescence-intensity curve is proportional to the amount of radicals that have recombined with one another, while the area between this curve and the straight line $I = I_0$ is proportional to the amount of radicals that have reacted with Mn^{2+}, or, equivalently, to the amount of manganese salt that has passed into another valence state. Figure 3 plots the dependence of $(I_0 - I)/\sqrt{I_0 I}$ on [Mn], calculated graphically from curve 1 of Fig. 1.

Fig. 3. Dependence of $(I_0 - I)/\sqrt{I_0 I}$ on [Mn], calculated graphically from curve 1 of Fig. 1

Fig. 4. 1 –kinetic curve of the change in chemiluminescence intensity in the nonstationary regime of the reaction; 2 –anamorphosis of curve 1 in the coordinates of equation (5)

graphically. Linearity is satisfied satisfactorily; from this graph the value $k_7/\sqrt{k_6} = 36\ (\mathrm{l/mol \cdot sec})^{1/2}$.

All the methods described above for treating the experimental results make it possible to determine only the relative rate constant for the interaction of $RO_2\cdot$ and $MnSt_2$. To obtain the absolute value of this quantity it is necessary to know the constant k_6 for the rate of recombination of RO_2 radicals. The chemiluminescence method makes it possible to find this quantity as well, in the case when the reaction proceeds in a nonstationary regime ([8]), i.e., under a rapid change in the initiation rate from $(w_i)_1$ to $(w_i)_2$. Integrating the equation $d[\mathrm{RO_2}\cdot]/dt = w_i - k_6[\mathrm{RO_2}]^2$ and substituting the value of $[RO_2]$, expressed through the intensity of chemiluminescence, we obtain

$$\lg \frac{1+x}{1-x} - \lg \frac{1+x_1}{1-x_1} = \frac{2}{2.3}\sqrt{w_i k_6 t}, \tag{5}$$

where $x = \sqrt{I/I_2}$; $x_1 = \sqrt{I_1/I_2}$; I_1 and I_2 are the chemiluminescence intensities at the initial and final stationary states of the system, respectively.

The experiments were carried out as follows: into the reaction vessel, where at a given temperature a stationary process of initiator decomposition was taking place, a new portion of a solution of azobisisobutyronitrile in chlorobenzene was injected (Fig. 4, curve 1; the moment of injection is indicated by an arrow). Over 5-10 sec a change in the intensity of the luminescence is observed; then a constant chemiluminescence current is established, corresponding to the new stationary state of the reaction. Control experiments showed that injection into the reaction zone of a certain amount of cold solution and the mixing time do not substantially affect the kinetics of the nonstationary reaction. In the coordinates of equation (5), the kinetic curve of the nonstationary change in the chemiluminescence intensity is transformed into a straight line (Fig. 4, straight line 2). The value of the recombination rate constant was calculated as the geometric mean of five quantities (Table 1).

Table 1

w_i, 10^{-8} mol/l·sec	1.35	1.22	1.20	1.06	0.6	
k_6, 10^7 l/mol·sec	2.25	2.32	1.89	0.85	1.2	$k_{6\text{avg}} = 1.6$

If it is assumed that k_6 does not depend on temperature, then these experimental data make it possible to calculate the absolute rate constant of the reaction between $RO_2\cdot$ and $MnSt_2$ (in $(\text{l/mol}\cdot\text{sec})^{1/2}$): at 60°, $k_7 = 2.0\cdot 10^5$; at 70°, $2.4\cdot 10^5$; at 80°, $3\cdot 10^5$, or $k_7 = 2.8\cdot 10^8 \exp(-4800\ \text{kcal}/RT)$. The obtained values of the preexponential factor and activation energy are close to the corresponding quantities for the reaction of interaction of $RO_2\cdot$ radicals with strong inhibitors ([9]). The low value of the activation energy is noteworthy. As is known, the transition potential $Mn^{2+} \rightarrow Mn^{3+}$ is 1.5 eV, or 35 kcal. Apparently, the small activation energy of the interaction of $RO_2\cdot$ and $MnSt_2$ is explained by the fact that not an ionic but a heteropolar bond is formed.

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CITED LITERATURE

1. E. T. Denisov, N. M. Emanuel, *Usp. khim.*, **29**, 1409, 1960.
2. K. U. Ingold, *Chem. Rev.*, **61**, 6, 563 (1961).
3. V. M. Gol' dberg, L. K. Obukhova, N. M. Emanuel, *Neftekhimiya*, **2**, 229 (1962).
4. V. M. Gol' dberg, L. K. Obukhova, *Neftekhimiya*, **4**, 466 (1964).
5. R. F. Vasil' ev, A. A. Vichutinskii et al., *Tr. po khim. i khim. tekhnol.*, **1**, 1961, p. 44.
6. R. F. Vasil' ev, O. N. Karpukhin, V. Ya. Shlyapintokh, *DAN*, **125**, 106 (1958); *ZhFKh*, **35**, No. 2 (1961).
7. O. N. Karpukhin, V. Ya. Shlyapintokh, N. V. Zolotova, *Izv. AN SSSR, OKhN*, 1963, 1718, 1721.
8. A. A. Vichutinskii, *DAN*, **157**, 150 (1964).
9. L. A. Bugaenko, M. B. Neiman, N. Ya. Kaganskaya, *Tr. po khim. i khim. tekhnol.*, **1**, 1961, p. 31.
10. R. F. Vasil' ev, *DAN*, **144**, 143 (1962).

Note: Figure translations are in progress. See original paper for figures.