PHYSICAL CHEMISTRY

1964

SovietRxiv

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PHYSICAL CHEMISTRY

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CHEMILUMINESCENT METHODS FOR DETERMINING THE ABSOLUTE VALUE OF THE RATE CONSTANTS OF TERMINATION OF PEROXIDE RADICALS IN THE LIQUID PHASE

(Presented by Academician V. N. Kondrat' ev on January 27, 1964)

Low-temperature oxidation of hydrocarbons is usually accompanied by weak chemiluminescence ($^{1-3}$). The glow arises upon recombination of peroxide radicals (^{4,5}) and is associated with the emission of excited oxygen (^{6,7,19}) or ketone (^{18}) formed during recombination. Introduction into the system of certain luminescent substances (^{6,7,19}) (activators) intensifies the glow without affecting the rate of oxidation (^{8,9}). Transfer of energy to the activator reduces the quenching action of oxygen and of certain initiators (azobisisobutyronitrile (AIBN), bis-α-azoethylbenzene (AEB), etc.), which is due to the shorter lifetime of the excited activator compared with the recombination products. For activated chemiluminescence

$$I_{\text{chl}} = \chi f k_6 [\text{RO}_2]^2, \tag{1}$$

where χ is the enhancement coefficient of the glow due to the activator, f is the overall yield of unactivated chemiluminescence, k_6 is the termination constant, and $[\text{RO}_2]$ is the concentration of peroxide radicals. The quantitative relation between chemiluminescence and radical concentration has been repeatedly confirmed by experiments on determining the activation energies and decomposition constants of initiators (^{1}), by studies on quenching of chemiluminescence by inhibitors (^{10}), by comparing the glow intensity with the rate of oxygen consumption (^{11}), by investigation of the catalyzed oxidation of hydrocarbons (^{12}), etc. This relation makes it possible to determine the relative concentration of radicals from the glow intensity:

$$I_1/I_2 = [\text{RO}_2]_1^2/[\text{RO}_2]_2^2; \tag{2}$$

In the stationary regime

$$d[\mathrm{RO_2}]/dt = 0, \qquad [\mathrm{RO_2}]_{\mathrm{st}} = \sqrt{W_i/k_6}. \tag{3}$$

If at the initial moment a nonstationary concentration of peroxide radicals is created in some way, for example by a sharp change in the initiation rate $W_{i0} \to W_{i1}$, then

$$d[\mathrm{RO_2}]/dt = W_i - k_6[\mathrm{RO_2}]^2. \tag{4}$$

The solution of equation (4) will be

$$\text{for } W_i = 0 \qquad [\mathrm{RO_2}]_0/[\mathrm{RO_2}] - 1 = t\sqrt{k_6 W_{i0}}; \tag{5}$$

$$\text{for } W_i \neq 0 \qquad \ln\frac{([\mathrm{RO_2}]_\infty + [\mathrm{RO_2}])([\mathrm{RO_2}]_0 - [\mathrm{RO_2}]_\infty)}{([\mathrm{RO_2}] - [\mathrm{RO_2}]_\infty)([\mathrm{RO_2}]_0 + [\mathrm{RO_2}]_\infty)} = 2t\sqrt{k_6 W_{i1}}, \tag{6}$$

where $[\mathrm{RO_2}]_0$ is the radical concentration at $t = 0$, $[\mathrm{RO_2}]$ at time t, and $[\mathrm{RO_2}]_\infty$ the stationary concentration as $t \to \infty$. Passing from radical concentration to glow intensity*, using (2), we obtain

$$\sqrt{I_0/I} - 1 = t\sqrt{k_6 W_{i0}} \tag{7}$$

from (5), and

$$\ln\frac{(\sqrt{I_\infty} + \sqrt{I})(\sqrt{I_0} - \sqrt{I_\infty})}{(\sqrt{I} - \sqrt{I_\infty})(\sqrt{I_0} + \sqrt{I_\infty})} = 2t\sqrt{k_6 W_{i1}} \tag{8}$$

from (6).

* An analogous regime was apparently realized in the work of Shtauf ([19]), since his experimental curves of the decay of chemiluminescence intensity become straight in the coordinates $I^{-1/2}$–t.

In the present work it is proposed, for determining the absolute value of the rate constant for termination of peroxide radicals, to use the chemiluminescence accompanying a nonstationary oxidation regime, which was created by methods of photo-aftereffect and oxygen aftereffect.

I. Method of Photochemical Aftereffect

A hydrocarbon saturated with oxygen is irradiated with ultraviolet light, which creates a certain constant rate of initiation, $W_{i\phi} = \text{const}$. The illumination is then sharply interrupted (i.e., $W_i = 0$) and the kinetics of the decrease in the chemiluminescence intensity is observed. In this case formula (7), by which the value of k_6 was calculated, is valid.

Fig. 1. Schematic diagram of the apparatus for studying photo-aftereffect by means of chemiluminescence.
1 –illuminator (DRSh-250); 2 –condenser; 3 –heat filter; 4 –diaphragm; 5 –objective producing a parallel beam; 6 –filter (activator solution); 7 –shutter; 8 –thermostated cuvette; 9 –shutter before the photomultiplier; 10 –photomultiplier; 11 –synchronizer for the operation of shutters 7 and 9; 12 –amplifier; 13 –recording device.

The photo-aftereffect was studied with the apparatus shown in Fig. 1. A parallel beam of light illuminates a thermostated cuvette with the hydrocarbon being oxidized, containing a sensitizer (anthraquinone, $\sim 10^{-3}$ mol/liter) and an activator (9,10-dibromoanthracene (9), $\sim 10^{-3}$ mol/liter) (in this case the absorption of light in the system did not exceed 10%, and uniform generation of radicals was produced throughout the volume). After the stationary state was reached, $[\mathrm{RO_2}]_{\mathrm{st}} = \sqrt{W_{i\phi}/k_6}$, the illumination was interrupted and the shutter before the photomultiplier was opened; the photomultiplier recorded the kinetics of decay of the activated chemiluminescence (Fig. 2 A, 2). A filter (a solution of 9,10-dibromoanthracene in benzene, 0.02 mol/liter), ensuring complete absorption of short-wavelength radiation with $\lambda < 410$ mμ, was placed in front of the cuvette. The rate of photoinitiation was varied by changing the light flux with the aid of a diaphragm and a set of neutral light filters (HCl–HClO), possessing uniform absorption in the region $\lambda > 420$ mμ.

Fig. 2. A. 1 –phosphorescence of the system without oxygen, 2 –kinetics of chemiluminescence (I_{chl}) of oxidizing cumene after illumination is stopped ($W_{i\phi} = 5 \cdot 10^{-8}$ mol • l^{-1} • sec^{-1}), 3 –anamorphosis of curve 2. B –kinetics of chemiluminescence at $W_{i,\mathrm{dark}} = 6.0 \cdot 10^{-9}$ mol • l^{-1} • sec^{-1}, 2 –anamorphosis of curve 1.

The value of $W_{i\phi}$ was found by comparing the initial intensity I_0 with the luminescence of the system at a known initiation rate W_i:

$$W_{i\phi} = W_i I_0 / I_{W_i}. \tag{9}$$

Dicyclohexyl peroxydicarbonate (PC) was used as the initiator (which does not absorb in the near UV); for it [13]

$$W_i = 1.4 \cdot 2.7 \cdot 10^{15} e^{-29600/kT} [\mathrm{Y}], \tag{10}$$

Fig. 3. Kinetics of chemiluminescence after rapid saturation with oxygen. A—cumene + PC system ($t = 40°$), $W_i = 1.49 \cdot 10^{-8}$ mol $\cdot$ l^{-1} $\cdot$ sec^{-1}; B—ethylbenzene + AEB at 36°, $W_i = 1.75 \cdot 10^{-11}$ mol $\cdot$ l^{-1} $\cdot$ sec^{-1}; C—anamorphoses of curves A and B

Figure 1: Fig. 3. Kinetics of chemiluminescence after rapid saturation with oxygen. A—cumene + PC system ($t = 40°$), $W_i = 1.49 \cdot 10^{-8}$ mol $\cdot$ l^{-1} $\cdot$ sec^{-1}; B—ethylbenzene + AEB at 36°, $W_i = 1.75 \cdot 10^{-11}$ mol $\cdot$ l^{-1} $\cdot$ sec^{-1}; C—anamorphoses of curves A and B

where [Y] is the initiator concentration.

In order not to carry out special experiments to determine the initiation rate, we introduced the initiator (PC), producing W_i, into the system from the very beginning. The kinetics of chemiluminescence in this case is described by equation (8) (Fig. 2B, 1). From the value of the slope of straight line 3 in Fig. 2A and straight line 2 in Fig. 2B we find the value of the rate constant for termination of peroxide radicals. For cumene $k_6 = (3.3 \pm 0.5) \cdot 10^4$ l/mol $\cdot$ sec at 20°.

Fig. 3. Kinetics of chemiluminescence after rapid saturation with oxygen. **A**—cumene + PC system ($t = 40°$), $W_i = 1.49 \cdot 10^{-8}$ mol $\cdot$ l^{-1} $\cdot$ sec^{-1}; **B**—ethylbenzene + AEB at 36°, $W_i = 1.75 \cdot 10^{-11}$ mol $\cdot$ l^{-1} $\cdot$ sec^{-1}; **C**—anamorphoses of curves **A** and **B**.

II. The oxygen aftereffect method is based on instantaneous saturation of the system (hydrocarbon + initiator + 9,10-dibromoanthracene 10^{-3} mol/l) with oxygen, followed by recording the kinetics of establishment of the stationary concentration of peroxide radicals by means of chemiluminescence. At the moment of saturation, radicals $R\cdot$ are converted into $\mathrm{RO_2}\cdot$. The reaction

$$\mathrm{R} \cdot + \mathrm{O_2} \xrightarrow{\mathrm{k_2}} \mathrm{RO_2} \cdot$$

for most hydrocarbons, because of the large value of the constant k_2, proceeds rapidly and is not the limiting stage. Experimentally it is not possible to saturate the liquid with oxygen instantaneously, but the luminescence intensity is already independent of the oxygen concentration at $[\mathrm{O_2}] \geq 10^{-6}$ mol/l (10^{-3}-10^{-4} of the solubility of $\mathrm{O_2}$); i.e., the time for complete conversion $R \to \mathrm{RO_2}$ is much less than the time for establishment of the equilibrium oxygen concentration.

To prove that the work was being carried out not in the diffusion region of saturation, special experiments were performed in which the rate was varied—

the gas feed rate during saturation (by a factor of 10) and the oxygen concentration by diluting it with an inert gas (from 5 to 1000 times), which did not affect the kinetics of chemiluminescence.

When AIBN was used as the initiator, it was shown$^{(2)}$ that the cyanoisopropyl radicals formed cause oxidation only after oxygen addition, i.e., without oxygen $W_i = 0$, and with oxygen $W_i = \text{const}$; according to$^{(14)}$

$$W_i = 1.15 \cdot 1.58 \cdot 10^{15} \cdot e^{-30800/RT}[Y]. \tag{11}$$

In this case equation (8) is valid:

$$\ln\left[\frac{\sqrt{I_\infty}+\sqrt{I}}{\sqrt{I_\infty}-\sqrt{I}}\right] = 2t\sqrt{k_6 W_i}.$$

If the initiator radicals interact with the hydrocarbon even without oxygen, then $W_i = \text{const}$. In this case

$$Y \to r \xrightarrow{+RH} R\cdot \quad \text{and} \quad R\cdot + R\cdot \xrightarrow{k_4} \text{products (without oxygen).}$$

In the presence of oxygen, termination proceeds on peroxide radicals:

$$\mathrm{RO_2} + \mathrm{RO_2} \xrightarrow{k_6} \text{products.}$$

Consequently, without oxygen $[R]_{\text{st}} = \sqrt{W_i/k_4}$, and with oxygen $[\mathrm{RO_2}]_{\text{st}} = \sqrt{W_i/k_6}$. Because of the rapid saturation with oxygen, it may be assumed that $[R_{\text{st}}] = [\mathrm{RO_2}]_0$. It follows that

$$k_4 = k_6 I_\infty / I_0. \tag{12}$$

For cumene it was found that $k_4 \gg k_6$ (see Fig. 3A), and for ethylbenzene $k_4 > k_6$ (see Fig. 3B). The value I_0 can be determined both from the kinetic curve of chemiluminescence (Fig. 3B) and from the value a intercepted by line B, found from Fig. 3B:

$$I_0 = I_\infty \left[(10^a - 1)/(10^a + 1)\right]^2.$$

For ethylbenzene initiated by bis-α-azoethylbenzene

$$\left(W_i = 1 \cdot 0.66 \times 10^{15} e^{-32600/RT}[Y]\right)^{(10)},$$

in the temperature range 36-60°,

$$k_6 = (4 \pm 0.6) \times 10^7 \ \mathrm{l \cdot mol^{-1} \cdot sec^{-1}}$$

Fig. 4. Temperature dependence of the recombination constant of cumene peroxide radicals. Φ —photo-aftereffect method; PK and AIBN —oxygen-aftereffect method with different initiators; L —literature data (17)

Figure 2: Fig. 4. Temperature dependence of the recombination constant of cumene peroxide radicals. Φ —photo-aftereffect method; PK and AIBN —oxygen-aftereffect method with different initiators; L —literature data (17)

(according to (8)), and

$$k_4 = (2 \pm 0.3) \times 10^8 \ \mathrm{l \cdot mol^{-1} \cdot sec^{-1}}$$

(according to (12)).

Fig. 4. Temperature dependence of the recombination constant of cumene peroxide radicals. Φ —photo-aftereffect method; PK and AIBN —oxygen-aftereffect method with different initiators; L —literature data (17).

For cumene, the activation energy of recombination of peroxide radicals was determined to be 2.3 ± 0.3 kcal/mol (Fig. 4).

The oxygen-aftereffect method is simple and makes it possible to determine the absolute value of radical termination rate constants in the range 10^4–10^8 l/mol · sec, which gives reason to hope for its broad application.

The author expresses gratitude to V. M. Andreev, V. Ya. Shlyapintokh, and N. M. Emanuél' for valuable suggestions and interest in the work.

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Received
1 I 1964

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