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Fig. 1

Figure 1: Fig. 1

Abstract

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CHEMILUMINESCENCE ACTIVATED BY ANTHRACENE DERIVATIVES

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1. Recently, weak chemiluminescence has been recorded in many reactions (1), in particular in reactions of hydrocarbon oxidation (2,3). It has been shown (4,12) that introducing well-luminescing substances into the solution leads to an enhancement (activation) of chemiluminescence.

In the present work, activation by additions of luminophores—9,10-derivatives of anthracene, whose absorption and photoluminescence were studied in detail by one of us (5,6)—was investigated.

2. **Method.** The reaction was the oxidation of hydrocarbons, initiated by the decomposition of α, α'-azobisisobutyronitrile (2); the solvent was benzene; the hydrocarbons were cyclohexane and ethylbenzene*; the activators were anthracene and its 9,10-substituted derivatives**; the monochromator was according to Fasti (7,8).

Fig. 1. "Oxygen decays" during oxidation of 2% solutions of methyl oleate (*a*) and ethylbenzene (*b*) in benzene at 60°. 3a, 2b—without activator; 2a, 1a —0.33 and $1.8 \cdot 10^{-3}$ mole/L 9,10-diphenylanthracene; 1a—$\sim 10^{-5}$ mole/L 9,10-dibromoanthracene. The points show the transformation of curves 2 and 3 into curve 1.

3. The intensifying action of activators was explained by energy transfer (4,12). It must be taken into account, however, that activators can become involved in the reaction (be oxidized). It may therefore be assumed that the glow in the presence of activators is chemiluminescence of the activators themselves. This possibility is unlikely in light of the following facts: a) the intensifying action is antibatic to the chemical stability of the activators; b) upon gradual consumption of dissolved oxygen, a "decay" of the glow occurs (2), the form of which is strictly characteristic of the oxidation of the given hydrocarbon (Fig. 1). Introduction of an activator increases the intensity of the glow over the entire course of the

kinetic curve. The curves are readily transformed into one another, i.e., the form of the decay practically does not change and is determined by the reactivity of the hydrocarbon, not of the activator.

4. The chemiluminescence spectrum of oxidizing cyclohexane is a band with a poorly characteristic maximum in the region 430–450 mμ (Fig. 2). Introduction of an activator sharply changes the appearance of the spectrum, and it becomes identical with its fluorescence spectrum. Consequently, the energy of the reaction is transferred to the activator and brings it into the excited singlet state.
5. The action of identical anthracene derivatives on the chemiluminescence of oxidizing cyclohexane (Fig. 3A) and ethylbenzene (Fig. 3B) is qualitatively identical. The small quantitative differences (the smaller amplification coefficient in the case of ethylbenzene) are connected either with the different structure of the excited recombination products, or with their different concentrations.

In terms of their amplifying action, the activators differ very strongly (see Fig. 3), and they may be divided into two groups:

a) "Good" activators—bromoanthracene, dibromoanthracene, bromophenylanthracene, dichloroanthracene, diphenylanthracene. The amplification coefficient increases monotonically with increasing concentration.

b) "Poor" activators—anthracene, di-*n*-propylanthracene, and dimethylanthracene. The amplifying action is small; the amplification coefficient passes through a maximum, and at high concentrations quenching of the luminescence is observed.

6. It is still difficult to say what the indicated features are connected with. It may only be mentioned that the "poor" activators are photochemically active and not very chemically stable, whereas the "good" ones are inactive and chemically stable. Apparently, the quenching of chemiluminescence is the result of interaction of the activator with the excited energy donor.
7. It may be considered that in the case of "good" activators, quenching has little effect.

Table 1

Quantum yield of fluorescence of activators η_A and chemiluminescence amplification coefficient χ

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* Cyclohexane was purified by chromatography on aluminum oxide; ethylbenzene—by shaking with 10% oleum, solutions of potassium permanganate and sodium metabisulfite, water, drying over sodium, and vacuum distillation.

** Anthracene derivatives were purified by recrystallization and chromatography on aluminum oxide.

Activator	Dibromoanthracene	Bromophenylanthracene	Dichloroanthracene	Bromoanthracene	Diphenylanthracene
η_A	0.095	0.16	0.48	0.017	0.74
χ at $[A] = 2 \cdot 10^{-5}$ mol/l	12	7	3	1.7	1.3
χ at $[A] = 2 \cdot 10^{-4}$ mol/l	90	50	23	5	2.5
k_{PA}/f_P, (l/mol)	$6 \cdot 10^6$	$2 \cdot 10^6$	$2 \cdot 10^5$	$2 \cdot 10^6$	$1 \cdot 10^4$
k_{PA}^{rel}	600	200	20	200	1

It was found that, for them, the dependence of the amplification coefficient χ on the activator concentration $[A]$ obeys the equation

$$\frac{1}{\chi - 1} = b + \frac{c}{[A]}$$

(see Fig. 4), which is readily obtained from a scheme that takes into account the fate of the excited particles:

Process	Equation	Rate of process
Appearance of excited products*	$\mathrm{RO_2} + \mathrm{RO_2} \to \mathrm{P}^*$	$\eta_P^{\text{exc}} w_{\text{rec}}$
Emission (chemiluminescence)	$\mathrm{P}^* \to \mathrm{P} + h\nu$	$f_P[\mathrm{P}^*] = I_P$
Deactivation	$\mathrm{P}^* \to \mathrm{P}$	$d_P[\mathrm{P}^*]$
Energy transfer	$\mathrm{P}^* + \mathrm{A} \to \mathrm{P} + \mathrm{A}^*$	$k_{PA}[\mathrm{P}^*][\mathrm{A}]$
Emission (activated chemiluminescence)	$\mathrm{A}^* \to \mathrm{A} + h\nu'$	$f_A[\mathrm{A}^*] = I_A$
Deactivation	$\mathrm{A}^* \to \mathrm{A}$	$d_A[\mathrm{A}^*]$

* In the quadratic termination of peroxide radicals, an alcohol, a ketone, and O_2 are formed. In this process, 100–150 kcal/mol (4–7 eV) of energy is released, which is distributed among the indicated three particles. The symbol P denotes that one of them which is responsible for chemiluminescence (most likely, the ketone).

Here w_{rec} is the rate of recombination of $\mathrm{RO_2}$ radicals; $\eta_{\mathrm{P}}^{\text{exc}}$ is the fraction of recombination events leading to excitation,

$$\varkappa = \frac{I_{\mathrm{P}} + I_{\mathrm{A}}}{I_{\mathrm{P}}^0}; \qquad I_{\mathrm{P}}^0 = I_{\mathrm{P}} \quad \text{at } [\mathrm{A}] = 0;$$

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

$$b = \frac{\eta_{\mathrm{P}}}{\eta_{\mathrm{A}} - \eta_{\mathrm{P}}}; \qquad c = \frac{1}{\eta_{\mathrm{A}} - \eta_{\mathrm{P}}} \cdot \frac{f_{\mathrm{P}}}{k_{\mathrm{PA}}}; \qquad \eta = \frac{f}{f + d},$$

where f, d are the probabilities of emission and deactivation, respectively.

Fig. 2. Chemiluminescence spectra of oxidizing cyclohexane ($1a$); the same in the presence of activators ($2a, 3a, 4a$) and fluorescence spectra of activators ($2b, 3b, 4b$). Entrance slit 7 mm, exit slit 2 mm, amplifier time constant 20 sec, scanning rate 0.3 m/sec. A is the curve of the relative spectral sensitivity of the apparatus (in energy units)

From the parameters of the straight lines in Fig. 4 one can estimate the yield η_{P} and the ratio $k_{\mathrm{PA}}/f_{\mathrm{P}}$

$$\eta_{\mathrm{P}} = \frac{f_{\mathrm{P}}}{f_{\mathrm{P}} + d_{\mathrm{P}}} \simeq \frac{f_{\mathrm{P}}}{d_{\mathrm{P}}} = 10^{-3} \div 10^{-4}.$$

It follows that the overall low yield of chemiluminescence ($\eta_{\mathrm{P}}^{\mathrm{exc}} \cdot \eta_{\mathrm{P}} = 10^{-8}$—$10^{-10}$) is to a certain extent associated with the low emission yield of the excited product, but is mainly determined by the small efficiency of excitation $\eta_{\mathrm{P}}^{\mathrm{exc}}$.

The values of $k_{\mathrm{PA}}/f_{\mathrm{P}}$ and the relative probabilities of transfer are given in the last rows of Table 1 (accuracy ±50—100%). For the activators studied, they differ by 3 orders of magnitude.

8. Formally, the large differences in the enhancing action can be explained by the fact that different activators have strongly differing values of the energy-transfer probability k_{PA}.

It is much more difficult to propose a mechanism explaining such large differences in k_{PA} in a series of closely related compounds. Evidently this is not inductive-resonance energy transfer—according to the Galanin-Förster theory, the transfer probability is determined by the overlap integral of the emission spectra.

donor and absorption by the activator (10), while the latter are practically identical for different anthracene derivatives (5, 6). This is also nonabsorptive transfer—the intensity must be proportional to the fluorescence quantum yield of the activator; moreover, no enhancement of luminescence should occur.

Fig. 4

Figure 4: Fig. 4

Fig. 3. Dependence of the luminescence enhancement coefficient on the concentration of activators during oxidation of cyclohexane (A) and ethylbenzene (B) in benzene at 50°. $[O_2] = 3 \cdot 10^{-5}$ mol/l. Activators (the fluorescence yield is given in parentheses): 1—anthracene (0.22); 2—di-*n*-propylanthracene (0.60); 3—diphenylanthracene (0.74); 4—dibromoanthracene (0.095); 5—bromophenylanthracene (0.16); 6—dichloroanthracene (0.48); 7—dimethylanthracene (0.63), 8—bromoanthracene (0.017)

It cannot further be overlooked that the probability of transfer increases in proportion to the number of halogens in the activator molecule and to the atomic number of the halogen (see Table 1). It is known that the introduction of heavy atoms weakens the intercombination prohibition and increases the probability of triplet-singlet transitions. If one assumes that k_{pA} for the best of the activators used—dibromoanthracene—is $\sim 10^{10}$ l/mol • sec (pre-exponent of a bimolecular reaction), then $f_p = 10^3$ sec^{-1}, which is precisely characteristic of the triplet state. Triplet-singlet energy transfer was recently observed in solid solutions (11) and, possibly, it also occurs in our case.

Fig. 4. Curves 4, 5, 6, 8 of Fig. 3A and curve 4 of Fig. 3B (4′), replotted according to the equation $(\chi - 1)^{-1} = b + c[A]^{-1}$

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