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QUENCHING BY OXYGEN OF EXCITED STATES IN CHEMILUMINESCENT SOLUTIONS

(Presented by Academician V. N. Kondrat' ev on 27 VI 1963)

1. In works ($^{1-2}$), qualitative data were presented indicating the major role of secondary processes—quenching and energy transfer—in chemiluminescent solutions (oxidizing hydrocarbons). Energy transfer from the excited product (P) of the recombination of hydrocarbon peroxide radicals to activators (luminophores) was studied quantitatively in a model system: oxidizing hydrocarbon—anthracene derivatives (^{3,4}).

In the present work, the regularities of the quenching of chemiluminescence by oxygen have been studied, and it is shown that certain components of the chemical system serve as "natural" activators and quenchers.

2. **Method** (see also (^{5,12})). The reaction was the oxidation of ethylbenzene in benzene (an inert solvent), initiated by the decomposition of dicyclohexyl peroxydicarbonate (DCPD)* at 40°. To measure the dependence of the chemiluminescence intensity on the concentration of O_2, we used the fact that, during oxidation of a mixture preliminarily saturated with O_2, in a sealed vessel $[O_2]$ gradually decreases. The oxidation rate w_{O_2} is equal to (^{5}):

$$w_{O_2} = k_3 k_6^{-1/2}[\mathrm{RH}]\sqrt{2f\ k_0[\quad]} + \frac{1}{2}\left(2f\ k_0[\quad]\right), \tag{1}$$

where k_3 and k_6 are the rate constants of the elementary oxidation steps; [RH] is the hydrocarbon concentration; k_0 is the rate constant of the thermal decomposition of DCPD, f is the initiation efficiency (the probability that primary radicals escape from the "cage"). It follows from equation (1) that w_{O_2} does not depend on $[O_2]$ and, consequently, is constant over the course of the experiment. The value of $[O_2]$ at the start of the reaction ($[O_2]_0$) is calculated from solubility tables, and the moment of its complete disappearance t is determined from the abrupt drop in luminescence (Fig. 1). Therefore it is not difficult to

Fig. 1

Figure 1: Fig. 1

Figure 2

Figure 2: Figure 2

determine $[O_2]$ at any point of the kinetic intensity curve, and the time scan simultaneously serves as a scan with respect to the concentration $[O_2]$.

Fig. 1. a—Kinetic curves of intensity (I, II) and concentration (I', II') of O_2 during oxidation of ethylbenzene (0.78 mol/l in benzene), initiated by DCPD at 40°C. $[\quad] = 3.1 \cdot 10^{-2}$ (for I, I'), $5.25 \cdot 10^{-2}$ (for II, II') mol/l; b—curves I and II, replotted in the coordinates of equation (2).

3. Figure 1 shows two kinetic curves of chemiluminescence intensity corresponding to two different reaction rates (i.e.

$$C_6H_{11}O{-}C(=O){-}O{-}O{-}C(=O){-}OC_6H_{11}$$

for various concentrations of DCGPC. As the concentration $[O_2]$ decreases, its quenching action weakens and the intensity increases. In the lower part of Fig. 1, curves *I* and *II* are replotted in the coordinates of the Stern—Volmer equation:

$$\frac{I_0}{I} = 1 + k\tau_\mathrm{P}[O_2], \tag{2}$$

where I_0 and I are the intensities (photocurrents) of the unquenched and quenched luminescence, τ_P is the lifetime of the excited state P^*, and k is the rate constant of the process:

$$P^* + O_2 \xrightarrow{k} P + O_2. \tag{3}$$

Fig. 2. Decrease in the relative values of η (black circles) and τ_P (white circles, left-hand scale) and of the quantity $k\tau_\mathrm{P}$ (white circles, right-hand scale) in the course of the reaction; [DCGPC] = 0.088 mol/l

The quantity τ_P is determined by all processes of deactivation of the excited molecule P^*, except deactivation by oxygen, and is equal to:

$$\tau_\mathrm{P} = \frac{1}{f_\mathrm{P} + d_\mathrm{P} + \sum_i k_{Q_i}[Q_i]}, \tag{4}$$

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* DCPD, $C_6H_{11}O{-}C(=O){-}O{-}O{-}C(=O){-}OC_6H_{11}$, was kindly provided by L. M. Terman. The substance was recrystallized from acetone into water, washed with methanol, and dried under evacuation with a vacuum pump.

Figure 3

Figure 3: Figure 3

where f_P and d_P are the probabilities of intramolecular radiative and nonradiative transitions, k_{Q_i} are the quenching constants by other quenchers Q_i present in the solution. The value of $k\tau_\mathrm{P}$, within the scatter (±10%), does not depend on the concentration of DCGPC, which varied from 0.03 to 0.2 mol/l. In particular, as is seen from Fig. 1 b, it is the same for two experiments corresponding to Fig. 1 a. At the same time, it was observed that in an individual experiment $k\tau_\mathrm{P}$ decreases during the course of the reaction.

A parallel measurement of the reaction rate w_{O_2}, the value $k\tau_\mathrm{P}$, and the intensity I_0 made it possible to compare the relative changes in τ_P and in the yield $\eta_\mathrm{P} \sim I_0/w_{O_2}$, which a priori should be equal to $f_\mathrm{P}\tau_\mathrm{P}$ (4). Indeed, it follows from Fig. 2 that η_P and τ_P decrease with time, while proportionality between these quantities is preserved. Evidently, this effect is connected with the accumulation of reaction products (peroxides?), which have the properties of quenchers (cf. equation (4)).

Fig. 3. Dependence on [DCGPC] of the intensity of the unquenched luminescence (1, in arbitrary units), the decomposition constant of DCGPC (2), and I : [DCGPC] (3, in arbitrary units), proportional to the luminescence yield

4. Extrapolation to the beginning of the reaction gives the value $k\tau_\mathrm{P} = 2 \cdot 10^3$ l/mol. Values of k for quenching of singlet states in solutions are of the order of 10^{10} l/mol · sec (6, 7). There are few data on quenching by O_2 of triplet states, but the reported values are of the order of 10^9 l/mol · sec (8, 9). Using these data, we obtain for the lifetime τ_P of the excited state P^* the values 10^{-7} sec (if P^* is a singlet) and 10^{-6} sec (if P^* is a triplet). Taking into account that $\eta_\mathrm{P} = f_\mathrm{P}\tau_\mathrm{P}$ and that η_P, measured in the oxidation reactions of cyclohexane and ethylbenzene, is of the order of 10^{-3}–10^{-4} (4), we obtain $f_\mathrm{P} = 10^3$–10^4 sec^{-1} (for S), 10^2–10^3 sec^{-1} (for T). These values are typical

specifically to the triplet electronically excited state; the same values were obtained when estimating f_P by another, independent method (^{4}). Therefore we assume that the chemiluminescence in the oxidation of ethylbenzene is a radiative T—S transition in the acetophenone molecule; acetophenone is formed upon recombination of ethylbenzene peroxide radicals, together with 2-phenylethanol and O_2 (^{10}).

[chemical reaction scheme]

Let us note that the recombination process is sufficiently exothermic (100–150 kcal/mole) for a portion of the acetophenone molecules to be at the T-level (73.1 kcal/mole (^{11})).

5. Theoretically, the intensity of luminescence in the reaction under study

should be proportional to the rate of decomposition of DCPK (^{12}):

$$I_0 \sim \eta_P k_0[\mathrm{DCPK}]. \tag{5}$$

Experimentally, I_0 increased faster than DCPK (Fig. 3). The rate ω_{O_2} was measured by the chemiluminescent method of "oxygen decays" (^{5}), and k_0 was calculated from formula (1) using the values

$$k_3/\sqrt{k_6} = 2.56 \cdot 10^{-4}\ \mathrm{liter}^{1/2}\,\mathrm{mole}^{-1/2}\,\mathrm{sec}^{-1/2}$$

(^{13}) and $f_{\mathrm{cl}} = 0.7$ (^{14}).

It follows from Fig. 3 that the relative increase in luminescence yield $\eta \sim I_0/[\mathrm{DCPK}]$ exceeds the error limits of determining the constant k_0, which is independent of [DCPK] to within ±4%.*

This result can be explained if one assumes that DCPK has the properties of an activator, i.e., that a portion of the acetophenone molecules transfers the excitation energy to DCPK, which emits with a higher yield.

[Figure 4 plot]

Fig. 4. 1 –kinetic curve of luminescence during oxidation of ethylbenzene at 40° and [DCPK] = 0.19 mole/liter; 2 –the same with 10^{-4} mole/liter 9,10-dibromoanthracene; 3 –the same with $3 \cdot 10^{-2}$ mole/liter AIBN

6. Introduction into the chemiluminescing solution of components that can successfully compete with O_2 in the processes of interaction with P^* should weaken the quenching action of O_2. Indeed, an effective activator –9,10-dibromoanthracene–and a quencher–α,α'-azobisisobutyronitrile, $(\mathrm{CH_3})_2\mathrm{CNC{—}N} = \mathrm{N{—}CCN(CH_3)_2}$ (AIBN)–almost completely remove quenching by oxygen (Fig. 4, 2, 3). Obviously, in the first case this is connected with transfer of energy to the activator (A) and with the small τ_A ($\sim 10^{-9}$ sec, S—S transition), in the second–with the small τ_P, due to the increased concentration of the quencher (see formula (4)). These results explain why in those reactions where AIBN serves as the initiator,** O_2, as a rule, does not quench chemiluminescence (see, for example, Fig. 1 in (^{5})) and the increase in intensity lags behind the increase in [AIBN] (^{15}). In addition to O_2, oxidation products, and AIBN, chemi-

* The value $k_0 = 1.3 \cdot 10^{-5}$ sec^{-1} obtained by us in a mixture of 10% ethylbenzene in benzene lies between the values corresponding to pure benzene: $2.0 \cdot 10^{-5}$ sec^{-1} (^{16}), and pure ethylbenzene: $0.67 \cdot 10^{-5}$ sec^{-1} (^{14}).

** At a higher temperature. The decomposition constant of AIBN is approximately 30 times lower than the decomposition constant of DCPK, and at 40° its chemical action is insignificant in comparison with that of DCPK.

luminescence is also quenched by other components of the system—the solvents and the hydrocarbons themselves. Quenching is one of the reasons for the low intensity of the glow in liquid-phase oxidation reactions and the principal reason for the short lifetime of the excited state.

Note added in proof. Recently[17] a value was obtained for the lifetime of the triplet state of acetophenone in hexane at room temperature. It is $3.6 \cdot 10^{-7}$ sec, which is close to our estimate.

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REFERENCES

1. R. F. Vasil' ev, A. A. Vichutinskii, *ZhFKh*, **36**, No. 8, 1799 (1962).
2. R. F. Vassil' ev, *Nature*, **196**, No. 4855, 668 (1962).
3. R. F. Vasil' ev, A. A. Vichutinskii, *Izv. AN SSSR, Ser. Fiz.*, **27**, No. 6 (1963).
4. R. F. Vasil' ev, A. A. Vichutinskii, A. S. Cherkasov, *DAN*, **149**, No. 1, 124 (1963).
5. R. F. Vasil' ev, A. A. Vichutinskii, *DAN*, **145**, No. 6, 1301 (1962).
6. T. V. Ivanova, G. A. Mokeeva, B. Ya. Sveshnikov, *Optics and Spectroscopy*, **12**, No. 5, 586 (1962).
7. A. S. Cherkasov, T. M. Vember, *Optics and Spectroscopy*, **6**, No. 4, 503 (1959).
8. G. Porter, M. Wright, *Disc. Farad. Soc.*, **27**, 18 (1959).
9. H. L. J. Bäckström, K. Sandros, *Acta chem. scand.*, **12**, 823 (1958).
10. G. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).
11. A. N. Terenin, V. L. Ermolaev, *Izv. AN SSSR, Ser. Fiz.*, **26**, No. 1, 21 (1962).
12. R. F. Vasil' ev, O. N. Karpukhin, V. Ya. Shlyapintokh, *DAN*, **125**, No. 1, 106 (1959).

13. V. F. Tsepalov, V. Ya. Shlyapintokh, *Kinetics and Catalysis*, **3**, No. 6, 870 (1962).

14. Z. I. Kulitskii, L. M. Terman et al., *Izv. AN SSSR, OKhN*, **1963**, No. 2, 253.

15. R. F. Vasil' ev, A. A. Vichutinskii et al., *Kinetics and Catalysis*, **4**, No. 3, 382 (1963).

16. G. A. Razuvaev, L. M. Terman, *ZhOKh*, **30**, No. 7, 2387 (1960).

17. F. Wilkinson, J. T. Dubois, *J. Chem. Phys.*, **39**, No. 2, 377 (1963).

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