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Abstract

Full Text

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THE MECHANISM OF CHEMILUMINESCENCE DURING THE OXIDATION OF ORGANIC SUBSTANCES IN SOLUTION

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In studying the mechanism of chemiluminescence, the principal problem is the identification of the excited particle. In the gas phase, identification from the vibrational-rotational structure of the spectra is sufficiently reliable. In solutions, the spectra of complex molecules are, as a rule, poorly characteristic; therefore it is necessary to use other characteristics: yield and lifetime.

We recorded spectra and estimated the lifetime τ_p and the quantum yield of radiation η_p during the oxidation of several hydrocarbons and their derivatives—in reactions accompanied by weak chemiluminescence (^{1}). The spectra were recorded on a photoelectric light-intensity spectrometer (^{2}); the receiver was an FEU-39 photomultiplier, sensitive in the region 3000-6300 Å. The quantum yield was determined from the laws governing energy transfer to luminophore activators (^{3}). The lifetime was estimated from the quenching of chemiluminescence by oxygen (^{4}). The oxidation reaction was carried out in benzene and chlorobenzene solutions. A constant reaction rate was maintained by thermal decomposition of the initiators—azobisisobutyronitrile and dicyclohexyl peroxydicarbonate (^{4}). The substances were purified by standard methods (^{3,4}).

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

Fig. 1. Chemiluminescence spectra during the oxidation of ethylbenzene *(1)*, cyclohexane *(2)*, *n*-decane *(3)*, and methyl ethyl ketone *(4)* at 60-65°. Entrance slit width 7 mm, exit slit 2 mm, with dispersion 20 Å/mm. *4′*—photoluminescence spectrum of diacetyl (according to data of work (7)). Along the ordinate —quantum spectral intensity on the frequency scale (in arbitrary units for each experiment).

During the oxidation of organic substances by oxygen, excited products are formed in elementary reactions of recombination (disproportionation) of peroxy radicals. The products of these reactions are carbonyl compounds, alcohols, and molecular oxygen, and the heat effect is 100-120 kcal/mol. It was shown in work (4) that the chemiluminescence of oxidizing ethylbenzene is triplet-singlet emission of acetophenone, $CH_3COC_6H_5$. It could be expected that, during the oxidation of other organic substances, the corresponding ketones would also be excited; for example, for cyclohexane—cyclohexanone $C_6H_{10}O$, for decane—decanone $C_{10}H_{20}O$, for methyl ethyl ketone—diacetyl $CH_3CO \cdot CO \cdot CH_3$. Comparison of the chemiluminescence spectra (Fig. 1) with the level positions of ketones known from the literature (Fig. 2) confirms this conclusion.* Especially

The oxidation of methylethyl ketone is characteristic: according to chemical data, the product of this reaction is diacetyl (6), and in the chemiluminescence spectrum the vibrational structure characteristic of the photoluminescence spectrum of diacetyl is repeated (cf. curves 4 and 4′ in Fig. 1); the lower resolution may be explained by the broad slit (equivalent to 700 cm^{-1}) and the elevated temperature.

The luminescence of diacetyl has been studied rather well (7). The triplet state of this substance has an exceptionally long lifetime in solution—up to 10^{-3} sec in well-purified solvents. Therefore, if triplet diacetyl is formed in the oxidation of methylethyl ketone, one should expect strong quenching of the chemiluminescence by oxygen. Indeed, this is observed experimentally (8). Deviations from the Stern–Volmer equation

Fig. 2. Scheme of the lower electronic levels of acetophenone (5), diacetyl (7), and molecular oxygen (12).

Fig. 3. Dependence of the ratio of the intensity of chemiluminescence quenched by oxygen to the unquenched intensity on the concentration of dissolved oxygen in the oxidation of methylethyl ketone (1) and ethylbenzene (2) in chlorobenzene.

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* We found no data on the chemiluminescence of cyclohexanone and decanone; however, it is known that aliphatic and aromatic ketones absorb and luminesce practically in the same regions of the spectrum (5).

$$I_0/I = 1 + k\tau_p[\mathrm{O}_2]$$

do not exceed 20% for a 40-fold change in the intensity I (Fig. 3). Using the value of the quenching constant k of triplet diacetyl by oxygen, $5.1 \cdot 10^9$ l/mol·sec (^{7}), we obtain for the lifetime of the chemiluminescence emitter the value $0.7 \cdot 10^{-5}$ sec. The shortening of the lifetime compared with the value 10^{-3} sec is due to the fact that in chemiluminescence it is impossible to satisfy the requirement of solvent purity, since the reaction requires a multicomponent mixture. The quenching effect in the oxidation of ethylbenzene is considerably smaller (Fig. 3), which is explained by the shorter lifetime of triplet acetophenone (of the order of 10^{-7} sec (^{4})).

The values of the quantum yield of radiation η_p also agree well with the concept of ketones as the emitters of the glow. The values of η_p are, for the oxidation of ethylbenzene, $5 \cdot 10^{-4}$, and of cyclohexane, $6 \cdot 10^{-4}$ (accuracy ±60%). They coincide in order of magnitude with the values obtained from the obvious formula $\eta_p = f_p\tau_p$, from independently measured lifetimes (several units of 10^{-7} sec (^{4})) and the probabilities of triplet-singlet radiation f_p, which are of the order of 10^3 sec^{-1} (^{5}). The yield η_p in the oxidation of methylethyl ketone was not determined in the present work; an estimate gives a rather high value,

$$\eta_p = f_p\tau_p = 10^3 \cdot 10^{-5} = 10^{-2},$$

and this agrees with the comparatively high experimentally established intensity of chemiluminescence, proportional to η_p:

$$I = \eta_p\eta_p^{\mathrm{exc}}\omega;$$

Here w is the rate of recombination or the rate of excitation; η_p^{exc} is the quantum yield of excitation or the probability of formation of an excited reaction product.

On the whole, the results presented show that chemiluminescence in the visible region during the oxidation of organic substances is a radiative transition in molecules of carbonyl compounds—the products of recombination of peroxy radicals. In this reaction molecular oxygen may also be excited, but its chemiluminescence (the transition $^1\Sigma_g^+ \to {}^3\Sigma_g^-$, Fig. 2) lies in the red region of the spectrum (^{9}).

The overall quantum yield of chemiluminescence, $\eta_{\mathrm{ch}} = \eta_p\eta_p^{\mathrm{exc}}$, is low (of the order of 10^{-10} for cyclohexane and decane, 10^{-9} for ethylbenzene, 10^{-7} for methylethyl ketone) and is determined mainly by the low value of the excitation yield, which is not difficult to estimate if the overall chemiluminescence yield η_{ch} and the emission yield η_p are known,

$$\eta_p^{\mathrm{exc}} = \eta_{\mathrm{ch}}/\eta_p.$$

The values of η_p^{exc} are of the order of 10^{-6}. Excited molecules are formed at the rate $\eta_p^{\text{exc}} w$, and disappear at the rate $[P^*]/\tau_p$; in the steady state these rates are equal. Hence, knowing the reaction rate w (usually of the order of $10^{-7} \div 10^{-6}$ mole/l • sec), one can estimate the steady-state concentration of excited molecules

$$[P^*] = \eta_p^{\text{exc}} \cdot w \cdot \tau_p = 10^{-20} \div 10^{-19} \text{ mole/l} = 10 \div 10^2 \text{ molecules/cm}^3.$$

The concentration proves to be very low, and this agrees with the low brightness of the glow:

$$I = f_p[P^*] = 10^3 \cdot (10 \div 10^2) = 10^4 \div 10^5 \text{ photons from 1 cm}^3 \text{ in 1 sec.}$$

The low probability of population of the electronic level in the reaction is most likely due to the nature of the energy distribution among the products, which results in the energy concentrated in most molecules being insufficient for excitation.

The low value of the excitation yield in recombination reactions is not connected with the operation of Wigner's rule, which requires conservation of the total spin of the system; as is evident from the equation of the excitation reaction, Wigner' s rule is obeyed for all conceivable combinations of product multiplicities,

$$\begin{array}{ccccc} \text{RO}_2 + & \text{RO}_2 \rightarrow & \text{ketone} + & \text{O}_2 + & \text{alcohol} \\ (1/2) & (1/2) & (0 \text{ or } 1) & (0 \text{ or } 1) & (0 \text{ or } 1) \end{array}$$

(the numbers in parentheses are spin values).

Therefore the products may be formed both in the triplet and in the singlet state. The fact that the chemiluminescence emitter in the oxidation of ethylbenzene is triplet acetophenone is due only to the rapid conversion, characteristic of this substance, from the singlet state to the triplet state ([5]), whereas in the reaction, apparently, both states are populated. In the oxidation of methylethyl ketone, transitions are observed from both the triplet and the singlet state, and the spectrum repeats the photoluminescence spectrum of diacetyl (cf. Fig. 1), which is a superposition of fluorescence and phosphorescence ([7]).

Thus, the structure of the spectrum is determined not by the portion of energy released (it is practically the same for all hydrocarbons), but by the luminescent properties of the excited product and by the processes of energy redistribution preceding emission. Therefore the presence of several maxima in the chemiluminescence spectrum does not necessarily indicate the parallel occurrence of several chemiluminescent reactions with different thermal effects and different products.

The quantum yield of excitation has the meaning of the probability of formation of one of the products of an exothermic elementary act in a definite energy state. This quantitative characteristic representa-

is of great interest for the theory of elementary chemical reactions, for understanding the processes governing the distribution and redistribution of energy among products. At present these questions are being intensively developed as applied to reactions of simple molecules in the gas phase ([10,11]). As applied to reactions in solutions, this work has not yet been begun. We hope that systematic measurements of the excitation yields of the products of liquid-phase reactions (ketones, oxygen in the oxidation of similar compounds) will provide much of value for the theory of elementary reactions in solutions.

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CITED LITERATURE

1. R. F. Vasil' ev, A. A. Vichutinskii, DAN, **142**, No. 3, 615 (1962).
2. R. F. Vasil' ev, T. N. Zhukova, S. M. Petukhov, *Optiko-mekhanich. prom.*, No. 3, 2 (1963).
3. R. F. Vasil' ev, A. A. Vichutinskii, A. S. Cherkasov, DAN, **149**, No. 1, 124 (1963).
4. R. F. Vasil' ev, I. F. Rusina, DAN, **153**, No. 5, 1101 (1963).
5. V. L. Ermolaev, *Optika i spektroskopiya*, **1**, 523 (1956).
6. G. E. Zaikov, Z. K. Maizus, N. M. Emanuel', DAN, **140**, No. 2, 405 (1961).
7. H. L. J. Bäckström, K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958); **14**, 48 (1960).
8. R. F. Vassil' ev, *Nature*, **196**, No. 4855, 668 (1962).
9. A. U. Khan, M. Kasha, *J. Chem. Phys.*, **39**, No. 8, 2105 (1963).
10. J. C. Polanyi, S. D. Rosner, *J. Chem. Phys.*, **38**, No. 4, 1028 (1963).
11. H. B. Palmer, W. J. Miller, *J. Chem. Phys.*, **38**, No. 1, 278 (1963).
12. G. Herzberg, *Spectra and Structure of Diatomic Molecules*, Moscow, 1949.