- 4. O. L. Gijzeman and F. Kaufman, J. Chem. Soc., Faraday Trans. 2, 69, 721 (1973).
- 5. K. C. Wu and A. M. Trozzolo, J. Phys. Chem., 83, 3180 (1979).
- 6. B. Stevens, K. L. Marsh, and J. A. Barltrop, J. Phys. Chem., 85, 3079 (1981).
- 7. G. P. Gurinovich and K. Salouhiddinov, Chem. Phys. Lett., 85, 9 (1982).
- 8. A. P. Darmanyan, Chem. Phys. Lett., 86, 405 (1982).
- 9. J. A. Howard and K. U. Ingold, J. Am. Chem. Soc., 90, 1056 (1968).
- 10. P. M. Merkel and D. R. Kearns, Chem. Phys. Lett., 12, 120 (1971).
- 11. P. B. Merkel and D. R. Kearns, J. Am. Chem. Soc., 94, 1029 (1972).
- 12. D. R. Adams and F. Wilkinson, J. Chem. Soc., Faraday Trans. 2, 68, 586 (1972).
- 13. P. B. Merkel and W. G. Herkstroeter, Chem. Phys. Lett., 53, 350 (1978).
- 14. K. C. Wu and A. M. Trozzolo, J. Phys. Chem., 83, 2823 (1979).
- 15. V. Ya. Shlyapintokh and V. B. Ivanov, Usp. Khim., 45, 202 (1976).
- 16. P. B. Merkel and D. R. Kearns, J. Am. Chem. Soc., 94, 7244 (1972).
- 17. J. A. Howard and G. D. Mendenhall, Can. J. Chem., 53, 2190 (1975).
- 18. H. Furue and K. E. Russell, Can. J. Chem., 56, 1595 (1978).
- 19. A. A. Krasnovskii, Biofizika, 22, 927 (1977).
- 20. K. I. Salokhiddinov, I. M. Byteva, and G. P. Gurinovich, Zh. Prikl. Spektrosk., <u>34</u>, 892 (1981).
- 21. T. A. Jenny and N. J. Turro, Tetrahedron Lett., 23, 2923 (1982).
- 22. A. P. Darmanyan, T. Vidoczy, and D. Gal, Proceedings of 8th IUPAC Symposium on Photochemistry, Seefeld (1980), p. 114.
- 23. T. R. Graffiths and D. C. Pugh, Coord. Chem. Rev., 29, 129 (1979).
- 24. R. C. Weast (ed.), Handbook of Chemistry and Physics, CRC Press, Cleveland (1977-1978).

CHEMILUMINESCENCE IN THE OXIDATION OF UNSATURATED ORGANIC COMPOUNDS IN SOLUTION

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The oxidation of organic materials by molecular oxygen in solution is often accompanied by low-intensity chemiluminescence (CL) [1]. In [2, 3] the quantitative properties of CL were obtained for the oxidation of alkylaromatics and of some other hydrocarbons that are oxidized at a secondary carbon atom. The present work is a study of CL in the oxidation of unsaturated compounds.

In the quantitative study of CL, certain additives are added to the solution of hydrocarbon to be oxidized, and the change in CL intensity, I, is followed [4]. The activators, A - strongly chemiluminescent acceptors of electron excitation energy - intensify CL. This permits the photophysical parameters to be determined: Φ_p , the yield; f_p , the rate constant, of the light emission; and $k_{e.t.}$, the rate constant of energy transfer. Addition of the quencher Q enables the actual lifetime of the CL emitter, τ_p , to be determined; dissolved oxygen can act as quencher. The addition of an initiator, a source of free radicals, makes it possible to obtain a definite rate of CL excitation, and to obtain Φ^* , the excitation yield, and Φ_{CL} , the absolute CL yield, which is equal to $\Phi_p \Phi^*$.

In the oxidation of RH_2 hydrocarbons that contain secondary C-H bonds, the source of CL excitation is the decomposition of tetroxide that forms when peroxide radicals meet, and the primary excitation carrier (i.e., CL emitter) is a carbonyl compound, R = 0 [1-3].

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Scheme 1

$$2\text{HROO} \stackrel{K}{\rightleftharpoons} \text{HROOOORH} \stackrel{k}{\rightarrow} \text{HROII} + O_2 + (1 - \Phi^*) \text{R} = 0 + \Phi^* \text{R} = 0^*$$
$$\text{R} = 0^* \stackrel{/\text{p}}{\rightarrow} \text{R} = 0 + h\nu_{\text{p}}$$
$$Q + R = 0^* \stackrel{k_{q}}{\rightarrow} \text{R} = 0 + Q$$
$$A + R = 0^* \stackrel{k_{e,t}}{\rightarrow} \text{R} = 0 + A^*$$
$$A^* \stackrel{q_{A}}{\rightarrow} A + h\nu_{A}$$

here k_q is the quenching rate constant, and ϕ_A is the quantum yield of activator luminescence. As follows from this scheme, the intensities of the total, direct, and activated CL are expressed by the following equations:

$$I = I^{\rm p} + I^{\rm A} \tag{1}$$

$$I^{\mathrm{P}} = \Phi_{\mathrm{CL}} w = \Phi_{\mathrm{P}} \Phi^* w \tag{2}$$

$$I^{\mathbf{A}} = \varphi_{\mathbf{A}} \Phi_{\mathbf{e},\mathbf{t}} \Phi^* \boldsymbol{w} ; \qquad (3)$$

here w is the rate of formation of R = 0 product; and $\Phi_{e.t.}$ is the yield of energy transfer.

$$w = w_i/2$$

$$w_i = k_6 [\text{HROO}]^2 = kK [\text{HROO}]^2 = 2f_{\text{CL}} k_0 [\text{Initiator}]$$

$$\Phi_{\text{e.t}} = k_{\text{e.t}} \tau_{\text{P}} [\text{A}]/(1 - k_{\text{e.t}} \tau_{\text{P}} [\text{A}]);$$
(4)

here w_i is the initiation rate; k_6 is the rate constant for chain breakage; k_0 is the rate constant for overall decomposition of initiator; f_{CL} is the efficiency of initiation; and $\phi_{e,t}$ is the yield of energy transfer.

In the absence of an initiator (w = 0) CL is negligible, the inhibitor antioxidants suppress CL almost completely ([HROO] = 0), and activators such as anthracene derivatives of europium complexes are chemically inert and only increase CL intensity without affecting the kinetics ($\varphi_A >> \varphi_I$; φ_e , approaches unity as the activator concentration increases).

In the present work we have tried to clarify the extent to which the above simple scheme is applicable to the oxidation of unsaturated hydrocarbons, and to determine the quantitative properties of CL excitation and emission. We studied the CL of sixteen unsaturated hydrocarbons. Data on the CL of four olefins are contained in the previous communication [5].

EXPERIMENTAL

The photometric apparatus, the working procedure, and the methodology of the determination of the quantitative properties of CL have been described in [4]. Most of the unsaturated hydrocarbon samples were obtained from the K. Schorlemmer Technical University, Merseburg, German Democratic Republic. Cyclohexene was synthesized by dehydration of cyclohexanol with orthophosphoric acid and then redistilled. The materials were stored in evacuated and sealed ampuls. Benzene and chlorobenzene were the solvents. The tests were carried out at 50 and 60°C.

DISCUSSION OF RESULTS

In olefin oxidation, CL behaves quite differently than in the oxidation of secondary hydrocarbons, and it must be concluded that there are several routes of CL excitation.

First of all, a perceptible CL is recorded in the absence of initiator and activator; during this time its intensity is practically constant. We call it inherent CL. The addition of an initiator that decomposes to radicals induces radical oxidation and invariably increases CL intensity. The contributions of initiated and inherent CL are different for different olefins. Below we shall discuss each component of CL, as exemplified by those olefins for which it is most distinctly exhibited. Inherent CL. The level of inherent CL is low, and depends on the "history" of the sample. For most hydrocarbons, CL increases upon storage. Furthermore, some substances show a contrary effect. For example, the CL intensity of our sample of 4-octyne was originally 10⁷ photons/ml sec, but after several months storage it decreased to one-tenth of that value. The intensity of inherent CL increases with temperature and olefin concentration. Since the addition of an inhibitor does not suppress inherent CL, it can be concluded that this component is not a radical. Apparently the products of the molecular decomposition of unstable impurities that accumulate during storage or even synthesis are CL emitters. The low intensity hinders the detailed study of the mechanism of inherent CL and its use. As is well known, in such cases it is appropriate to use activators.

Effect of Activators, Inhibitors, and Initiators. The most efficient CL activator in the oxidation of alkylaromatic hydrocarbons is a chelate of trivalent europium, $Eu(TTA)_3$ Phen (TTA is thenoyltrifluoroacetonate ion; Phen is 1,10-phenanthroline) [2]. Its high efficiency is related to the fact that energy transfer to the ligand complex and then to the central ion takes place at each encounter with the energy donor, and to the high quantum yield of lumin-escence, from 20 to 7% in the 25-60°C range [4].

Addition of the chelate to the olefin solution causes a jump in CL intensity, just as in the oxidation o- alkylaromatic hydrocarbons. There is, however, a substantial difference, viz., that the intensity does not remain constant, but falls after several minutes to a limit, I_{lim}^{ch} . We call this component the rapid component of activated inherent CL, and the limit that is reached after the rapid component disappears we call the slow component of activated inherent CL. Such nomenclature is justified because I_{lim}^{ch} is not constant, but slowly increases.

A definite fraction of the slow component is due to its origin in a radical reaction, because it can be suppressed by inhibitors, viz., radical CL (with intensity I_{rad}^{ch}). But there is still a component, which we call molecular CL (I_{mol}^{ch}). All this is illustrated in Fig. 1, which shows qualitatively the reaction of the system when activator, inhibitor, and initiator are added. The contribution of the radical component of activated CL increases when an initiator is added to the solution; the CL intensity depends linearly on the initiator concentration.

This picture of olefin CL kinetics and response to various additives is typical of all the compounds studied, although the contributions of the individual CL components varies substantially; this is shown in Table 1 for initiated CL. For comparison the table includes notation, cyclohexane, and ethylbenzene. The relative intensity, I_{rel}^{ch} , of radical CL for alkenes is very much lower than for alkanes. We note that the ratio $I_{mol}^{ch}/I_{rad}^{ch}$ must decrease with increasing initiation rate, and refers only to a particular value thereof, whereas I_{rel}^{ch} is obtained by calculation of actual CL intensities at the same initiation rate, and is therefore independent of the latter.

The molecular component increases, but after addition of inhibitor or removal of 0_2 it decreases. Such behavior has been explained by the formation [5], in a radical reaction, of unstable peroxide compounds (it was suggested that they were dioxetanes), which upon molecular decomposition give electron-excited carbonyl products.

Rapid Component of Activated Inherent CL. Olefin CL is intensified not only by the europium chelate, but also by other activators such as 9,10-diphenylanthracene (DPA) and 9,10dibromoanthracene (DBA). In these cases the intensification coefficient is substantially less, but the important point is that after a flash there is no decrease of intensity. Evidently in the case of the chelate the phenomenon amounts to more than just the physical process of energy transfer. A natural alternative explanation is the formation of a complex between the chelate and the peroxide that is always present in an actual sample. Decomposition of peroxide in the complex can excite the chelate by one of the following mechanisms: (a) direct excitation of the chelate during decomposition; (b) direct excitation of the decomposition product, followed by energy transfer to the chelate; (c) supplementary initiation: formation of free radicals during decomposition, their conversion to peroxide radicals, formation of tetroxide by the latter, and decomposition of tetroxide to give an electron-excited product, viz., a ketone, which transfers energy to the chelate.

Mechanism (c) can easily be eliminated because the characteristic CL flash is also observed when the inhibitor is added to the solution before the activator.



Fig. 1. Effect of activator, inhibitor, and initiator on CL kinetics.

TABLE 1.	Re	lative	Inten	sity d	of C	hemilum	inesco	ence	Activ	ated	by	Euro	opiu	m Cł	nelate
$(2 \cdot 10^{-4})$	mole	/liter)	and	Ratio	of	Molecul	ar and	1 Rad	lical	Compo	nen	ts :	in I	niti	ated
Oxidatio	on of	Unsatu	rated	Compo	ound	s (20%	in Chi	Lorob	enzen	e) at	: 50	°C*			

Compound	Туре	of radical	Ich rel, %	I ^{ch} mol/I ^{ch} , %
Cyclopentene	sec.		15	12
Cyclohexene	11		65	2
1-Hexene	prim., sec.		7	8
Tetramethylethylene	prim., tert.		2	61
2-Methy1-1-pentene	prim., sec.,	tert.	11	18
Norbornene	sec.		53	60
1-Pentene	prim., sec.		13	5
2-Methyl-1-hexene	prim., sec.,	tert.	13	4
4-Octyne	prim., sec.,	tert.	90	34
1-Octene	prim., sec.		15	3
cis-4-Octene	prim., sec.		19	37
trans-4-Octene	prim., sec.		5	36
2-Ethy1-1-hexene	prim., sec.,	tert.	49	2
2,4,4-Trimethyl-l-				
pentene	prim., sec.,	tert.	5	27
2,4,4-Trimethy1-2-				
pentene	prim., sec.,	tert.	5	33
3-Propy1-3-pentene	prim., sec.,	tert.	3	2
n-Octane	sec., prim.		240	-
Cyclohexane	sec.		1300	-
Ethylbenzene	prim., sec.		370	-

*Solution saturated with air. At 100% I^{ch}_{rel}, CL intensity taken in absence of hydrocarbon; intensities are relative to same initiation rate. Ratio of molecular to radical component corresponds to $6.0 \cdot 10^{-3}$ mole/liter of AIBN initiator and 20 vol.% of hydrocarbon. Prim, primary; sec, secondary; tert, tertiary.

The results for our olefins agree qualitatively with mechanism (a): after addition of chelate, the maximum ("starting") CL intensity is proportional to the concentration of chelate or hydrocarbon in the region where the latter values are small (we believe that along with hydrocarbon we are adding to the solution a proportional amount of "historical" peroxide), and then it approaches a limit; the effective rate constant increases with saturation as chelate concentration increases. As for mechanism (b), we must take into account that if the rate constant of energy transfer is close to the diffusional, then energy transfer occurs at each encounter of excited product with chelate. But immediately after decomposition of the complex, the peroxide decomposition product and the chelate are essentially in contact, so that energy transfer is more probable in the chelate cage; that is, to a molecule that is a component of the complex, rather than to one to which the product must first diffuse. This circumstance prevents us from distinguishing between mechanisms (a) and (b). In any case the final step is the emission of light by a europium ion; this is evidenced by the characteristic spectrum, which is a set of narrow bands of which the most intense is located at 612 nm. It is possible that complex formation amounts to replacement of the ligands of the europium chelate by peroxide molecules. We observed CL flashes when the chelate was introduced into a solution of peroxides that were potential complex formers, i.e., containing C=Ogroups. Such substances are di-tert-butyl peroxyoxalate, dicyclohexyl peroxydicarbonate, and ketodihydroperoxides, the oxidation products of methyl ethyl ketone. In the case of alkyl hydroperoxides, which are unable to replace ligands, the CL flash was not observed.

Radical Component of Activated Inherent CL. The suppression of CL by an inhibitor and its restoration after a time τ_{ind} (the induction period, see Fig. 1) permit the effective initiation rate [4] to be estimated. For the inhibitors that we used, viz., α -tocopherol and 1,2-bis(4-dimethylaminophenyl)-1,2-diphthaloylethane [6], w = 2[Inhibitor]/ τ_{ind} . The rates of inherent initiation are low, 10^{-10} to 10^{-9} mole/liter.sec and lower. It can be presumed that the inhibitors are the hydroperoxides (P) that have accumulated up to the moment the inhibitor is added; then w = $2k_3[P]$. As is well known, hydroperoxide accumulation for long chains, initiated by their decomposition at constant rate k_3 , goes by the rule [7]:

 $\sqrt{[P]} = \sqrt{[P]_0} + k_2 [RH_2] \sqrt{k_3/2k_6}$

where $[P]_0 = \alpha[RH_2]$ is the concentration of peroxide in the hydrocarbon, which is proportional to hydrocarbon concentration, and k_2 and k_3 are the rate constants for chain lengthening and breaking. Then

$$\sqrt{w_i/[\mathrm{RH}_2]} = \sqrt{2k_3\alpha} + (k_2k_3t/\sqrt{k_6})\sqrt{[\mathrm{RH}_2]}$$

If in a series of tests at different hydrocarbon concentrations the time t from the start of the reaction to the addition of inhibitor is kept constant, then the dependence of $\sqrt{w_1/[RH_2]}$ on $\sqrt{[RH_2]}$ must be linear. It is shown for 4-octyne in Fig. 2; this material had an unusually high rate of inherent initiation, 10^{-9} to 10^{-7} mole/liter•sec.

Initiated CL. It follows from Table 1 that the yield of chelate-activated CL in the oxidation of unsaturated hydrocarbons initiated by azobisisobutyronitrile (AIBN) is lower than in the AIBN + solvent system. Figure 3 shows the fall in CL intensity with increasing concentration of cyclohexene or 1-heptene. For these compounds the contribution of the radical component to CL is very large (see Table 1), and the results below are on good agreement with a scheme of radical-chain oxidation, in which the excitation carriers are cyclohexenone and heptenone, the products of the disproportionation of peroxide radicals (see Scheme (1)).

Scheme 2





Fig. 2. Dependence of effective rate of inherent initiation on 4-octyne concentration (%) in benzene at 60° C, in the coordinates of Eq. (5).



Fig. 3. Dependence of CL intensity on concentration of (1) cyclohexene and (2) 1-heptene in benzene at 60° C. [AIBN] = $5.0 \cdot 10^{-4}$; [X] = $2.0 \cdot 10^{-4}$ mole/liter.

Fig. 4. Dependence of CL intensity on AIBN concentration in benzene solution of olefin (20 vol.%): (1) cyclohexene and (2) 1-heptene at $60^{\circ}C_{\bullet}$

The intermediate segment in Fig. 3 is undoubtedly related to the competitive disproportionation of the peroxide radicals of the initiator and the appearance of olefin radicals: detachment of hydrogen atoms or addition to the double bond (Scheme 2 for 1-pentene). Detachment of allylic hydrogen is most likely, but the scheme also shows other reactions, including detachment of a hydrogen from methyl, because even low concentrations of primary peroxide radicals can make a substantial contribution to chain breaking and possibly to CL excitation [8]. Comparison of the curves in Fig. 3 shows that the exchange of radicals is more efficient in cyclohexene than in 1-heptene; this is related to some extent to the different numbers of highly mobile allylic hydrogen atoms (4 and 2). The expected proportionality between intensity and initiator concentration is very well achieved (Fig. 4).

For those olefins without inherent initiation, the following values are in satisfactory agreement: the increase in CL intensity when initiator is added and the weakening in initiated CL when oxygen is removed from solution or when an inhibitor is added to the solution (the two latter operations reduce the peroxide radical concentration to zero). Thus, e.g., in the case of 2,4,4-trimethylpentene, the inherent CL at 50°C was 49 scale divisions; after addition of $3 \cdot 10^{-3}$ mole/liter of AIBN it increased to 104 divisions; and after removal of O_2 or addition of inhibitor it decreased to practically the starting value, 50 or 48 divisions. For 1-hexene the respective values were 8, 115, 9 and 13 divisions.

Thus, the radical component of initiated CL behaves exactly the same as CL in the oxidation of secondary hydrocarbons. The radical component can be distinguished by several methods, e.g., thermal decomposition of accumulated peroxide in the absence of O_2 , establishing a high concentration of initiator, and careful purification of samples. The distinguishing of the radical component has important consequences. Thus, if the radical component is determined by an initiation rate that is known to the experimenter, then the quantitative CL properties can be obtained (see below). Then the nonsteady-state CL methods can be applied [7], p. 73), and the rate constants of peroxide radical disproportionation can be determined; a separate article will be devoted to this subject.

Energy Transfer and the Nature of the Excited Products. When we analyze the system response to the addition of various activators, we can draw conclusions about the excited state of the donor and the excited reaction product. Table 2 shows the expected rate constants of energy transfer from singlet and triplet energy donors at the luminescence levels of the activators.

Dissolved oxygen quenches cyclohexene CL weakly; at $[0_2] \simeq 10^{-3}$ mole/liter, 10% in all. Hence, if we consider k_q to be diffusional we estimate the lifetime of triplet cyclohexenone $\tau p \approx 1 \cdot 10^{-8}$ sec, which is close to $6 \cdot 10^{-9}$ sec, the value obtained in [9]. If we also take into account that the rate constant k does not exceed the diffusional value 10^{10} liter/mole·sec, whereas $[A] = 10^{-4}$ to 10^{-3} mole/liter, then from Eqs. (1)-(4) we obtain

$$I^{\mathbf{A}} = \varphi_{\mathbf{A}} k_{\mathbf{e},\mathbf{t}} [\mathbf{A}] \Phi^* \tau_{\mathbf{P}} w \tag{6}$$

If we compare CL values for the oxidation of the same hydrocarbon at the same concentrations of different activators, then CL intensity must be proportional to $\varphi_A k_{e^-t^-} \Phi^*$.

If the energy donors are only singlets, then the CL intensities with activators DPA, DBA, and X are in the ratio 1:0.12:0.09; if the donors are only triplets, then the ratio is quite different, 1:25:400.

For all the olefins the CL intensification by the chelate was invariably greater than that by DPA and DBA; this is evidence that the molecules are predominantly in the triplet states. Moreover, the experimental values of the ratio deviate from those shown above for the cases of "pure" singlet and triplet. Thus, for the radical component of cyclohexene CL we obtained in two series of tests 1:0.3:1300, and 1:0.4:1080; and for 1-heptene, 1:0.15:330. Probably the energy transfer to DBA and DPA is endothermic (according to [9] the energy of the cyclohexenone triplet is 66-63 kcal/mole), and this creates a preference for energy transfer to the chelate, because the $k_{e.t.}$ rate constants for DBA and DPA are smaller than shown in Table 2. The relatively greater CL intensity with DPA than with DBA, on the other hand, is evidence for some contribution by the singlet state also. Using the methodology developed in [4], we determined the yields of excited triplet and singlet states for the radical component of CL (Table 3), and also the emission rate constants, $f_p \leq 2 \cdot 10^2 \text{ sec}^{-1}$. The latter value is typical of the triplet $n\pi^*$ state of carbonyl compounds [10].

Table 3 shows that the excitation and emission yields are an order of magnitude lower, whereas the quenching constant, $K^A = k_{e.t.^Tp}$ is of the same order of magnitude as the values previously found [2, 3] for saturated compounds. The yields of Φ_T^* and Φ_S^* are different for the molecular and radical components. Thus, in cyclohexene oxidation, the addition of an inhibitor suppresses chelate-activated CL by 98%, but DPA-activated CL only 17%; evidently the singlet yield is higher in the molecular reaction than in the radical reaction.

The intensity I_{rel}^{ch} in Table 1 refers to oxidation in chlorobenzene, where the CL yield is an order of magnitude lower than in benzene. This is related to the shorter lifetimes, which apparently are determined by the quenching of the triplet state of medium, so that τ_p does not vary much for different alkenes. Furthermore, the I_{rel}^{ch} values are CL intensities for the oxidation of different compounds but at the same concentration of activator X, and they refer to the same reaction rate. When we take this circumstance and Eq. (6) into account, we can expect that I_{rel}^{ch} will be approximately proportional to the excitation yield.

We can explain the large variations in I_{rel}^{ch} and their relatively low values as follows. In olefin oxidation the participation of many kinds of radicals is typical (see Scheme 2 and [11]). This leads to a wide variety of chain-breaking reactions, which, as might be expected, make different contributions both to the overall rate of chain breaking and the yield of CL excitation. Thus ϕ^* is some effective value, and formula (3) is better written as

$$I^{A} = \phi_{A} \sum_{i} {}^{i} \Phi_{e.t.} {}^{i} \Phi^{* i} \Phi_{chem w}$$

where ${}^{i}\phi$ are the relative contributions to the overall rate of various chain-breaking reactions that give excited products in various yields, ${}^{i}\phi*$. For some chain-breaking reactions the excitation yields can be low, and this explains why the effective excitation yields for olefins are very much lower than for alkanes (see Table 1).

TABLE 2. Energy of Acceptor Levels of Activators and Rate Constants of Energy Transfer to Them from Singlet and Triplet Donor Levels, and Quantum Yields of Luminescence Activators in Benzene at $60^{\circ}C$ [2]

Activator	E _A , kcal/mole	k _{e.t.} , liter/mole·sec	φ _Α
9,10-Diphenylanthracene	72 (S ₁)	$\sim_{10^{10}}$ (from singlet) $\sim_{2.40^6}$ (from triplet)	0,83
9,10-Dibromoanthracene	71 (S ₁)	$\sim 10^{10}$ (from singlet) $\sim 4.10^8$ (from triplet)	0,11
Eu(TAA)3Phen	$74 (S_1)$ 58 (T_1)	$\sim 10^{10}$ (from singlet) $\sim 10^{10}$ from triplet)	0,07

TABLE 3. Yields of Excited Triplet and Singlet States, Emission Yields of Primary Emitter, Stern-Vollmer Quenching Constants of Triplets by Chelate and of Singlet by 9,10-Diphenylanthracene during Oxidation of Hydrocarbons at 60°C

		1		Kch KDP			
Hydrocarbon	Φ_T^*	Φ_S^*	Ф <i>Р</i>	lite	liter/mole		
Cyclohexene 1-Heptene Cyclohexane Methyl ethyl kerope	$2,1\cdot10^{-3} \\ 1,6\cdot10^{-4} \\ 1,0\cdot10^{-2} \\ 5,2\cdot10^{-3}$	5,0·10-7 2,0·10-6	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c} 1,5\cdot10^{+2}\\ 2,7\cdot10^{2}\\ 5,0\cdot10^{2}\\ 3,0\cdot10^{3} \end{array}$			

Table 1 shows the types of radicals that can take part in the oxidation of a particular hydrocarbon. According to our data [8], the CL yield is low in chain breaking of tertiary and primary peroxide radicals, but high in the disproportionation of secondary peroxide radicals. Apparently it is precisely for this reason that I_{rel}^{Ch} is so low (2%) for tetramethylethylene. On the other hand, the intensity is relatively high for cyclohexene, which is oxidized through secondary radicals that are produced predominantly by removal of an allylic hydrogen [12]. CL intensity is also relatively high for norbornene and cyclopentene, which oxidize only through secondary radicals, and for some other compounds where along with primary and/or tertiary radicals, secondary peroxide radicals also take part in the reaction.

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CONCLUSIONS

In the oxidation of unsaturated compounds, certain processes that form various electronexcited products make various contributions to chemiluminescence (CL). In pure olefins there is no CL; in actual samples CL is due to traces of peroxides. In the initiated olefin oxidation the low CL intensity is due to the excitation yield and the low emission yield of the primary emitter, an alkenone. Activator-intensified CL can be used to determine the kinetics of the radical-chain oxidation of olefins.

LITERATURE CITED

- 1. R. F. Vasil'ev, Usp. Khim., 39, 1130 (1970).
- 2. V. A. Belyakov and R. F. Vasil'ev, Molecular Photonics [in Russian], Nauka, Leningrad (1970), p. 70.
- 3. V. A. Belyakov, R. F. Vasil'ev, and G. F. Fedorova, Izv. Akad. Nauk SSSR Ser. Fiz., <u>42</u>, 613 (1978).
- 4. V. A. Belyakov, R. F. Vasil'ev, and G. F. Fedorova, Khim. Vys. Energ., <u>12</u>, 247 (1978).
- 5. V. A. Belyakov, T. V. Filippova, S. Yu. Zasedatelev, and E. A. Blyumberg, Izv. Akad. Nauk SSSR, Ser. Khim., 1485 (1979).
- 6. L. M. Pisarenko, A. B. Gagarina, and N. M. Émanuel', Dokl. Akad. Nauk SSSR, 221, 640 (1975).
- 7. N. M. Émanuel', E. T. Denisov, and Z. K. Maizus, Chain Oxidations of Hydrocarbons in the Liquid Phase [in Russian], Nauka, Moscow (1965), p. 120.
- 8. V. A. Belyakov, R. F. Vasil'ev, and G. F. Fedorova, Dokl. Akad. Nauk SSSR, 239, 344 (1978).
- 9. P. DeMayo, A. A. Nicholson, and M. F. Tchir, Can. J. Chem., <u>48</u>, 225 (1970).

10. S. MacGlynn, T. Adzumi, and M. Kinoshita, Molecular Spectroscopy of the Triplet State [Russian translation], Mir, Moscow (1972), p. 268.

11. W. Pritzkow, R. Radeglia, and W. Schmidt-Renner, J. Prakt. Chem., 321, 813 (1979).

12. D. Van Sickle, F. Mayo, and R. Arluck, J. Am. Chem. Soc., 87, 4824 (1965).

ACID-BASE PROPERTIES OF 7-AZAINDOLINES

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The present article continues the cycle of investigations of the mechanism of photodissociation of 7-azaindolines in the condensed phase. A study of the influence of the nature of the solvent on the spectral and luminescent properties of 7-azaindolines showed, that the mutual location of the $n\pi^*$ and $\pi\pi^*$ levels, which determine practically all properties, depend to a large degree on the polarity of the solvent and its ability to form hydrogen bonds.

The mutual location of the $n\pi^*$ and $\pi\pi^*$ levels of the 7-azaindolines depends even more on the acidity of the medium. Let us point out that in media with different acidities four different ionic forms of 7-azaindolines can exist:



where R = H(I); $OCH_3(II)$.

The purpose of the present study was to identify the different acid-base forms of the 7-azaindolines and the conditions for the conversion to each other. The procedures used for the measurement of the absorption spectra and the kinetics of decay of short-lived intermediate products, and of the spectral and luminescent characteristics of the 7-azaindolines have been described in [1].

DISCUSSION OF RESULTS

As mentioned in [1], the 7-azaindolines represent with respect to their structure close analogs of 2-aminopyridines, the luminescent properties of which have been studied thoroughly in [2-7]. It is therefore convenient to discuss simultaneously the properties of both series of compounds.

The absorption spectra of the 7-azaindolines and 2-aminopyridines are very similar (Fig. 1); they depend in the same way on the properties of the solvent. The long-wave absorption bands of the 2-aminopyridines and 7-azaindolines correspond to the $\pi \rightarrow \pi * ({}^{1}A_{1} \rightarrow {}^{1}B_{2})$ -transition of pyridine, slightly disturbed and suffering a bathochromic shift under the influence of the amino group [2]. In alcohols and in water an increase in intensity and a bathochromic shift of this band is observed at low pH (see Fig. 1). This is due to protonation of the 7-azaindoline and 2-aminopyridine in the pyridine ring and formation of the cation

$$B + H^+ \rightarrow C^+$$

The fact that protonation takes place in particular in the ring and not in the amino group is confirmed by the bathochromic shift and the increase in the extinction coefficient of the long-wave absorption band and of the fluorescence, since in the protonation of theamino group a hypsochromic shift is observed as a rule [8] (see Fig. 1)

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