CHANGE IN THE RATE OF DECOMPOSITION OF DIOXETANES IN SULFOLANE SOLUTIONS IN THE TRANSITION FROM THE LIQUID TO THE SOLID PHASE

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The possibility of chemical reactions occurring in substances in a true solid state was long doubted. And while it is generally accepted that the rate of such reactions depends strongly on the crystal modifications of the solids, the question of the acceleration of reactions when a phase change occurs (the Hedvall effect) remains in dispute.

Similar problems arise in cryochemistry in studying processes occurring in the solid phase at low temperatures. Data reported in the literature [1] show that the question of the interrelationship between structural changes and the effectiveness of low-temperature chemical reactions is a rather complex one, and that further research is required to answer it.

In order to study chemical processes at a phase boundary in frozen solutions, including during phase transitions, we employed the phenomenon of low-temperature chemiluminescence (CL) [1, 2]. Many reactions are known to have what is termed a negative temperature coefficient, i.e., the reaction rate increases when the solvent freezes. Acceleration of a reaction is usually associated either with concentration of the reagents in the unfrozen regions of the solvent or with the catalytic activity of the surface of the crystalline phase [4, 5].

Employing as our model a unimolecular reaction, whose rate does not depend on the concentration of the substance or its nonuniformity during freezing, would allow us to eliminate from consideration effects caused by the nonuniformity of the distribution of the reagents.

In the present work we used the method of CL to study the effect of the phase transitions of the solvent on the rate of the unimolecular reaction of the thermal decomposition of tetramethyl-1,2-dioxetane (I).

A special feature of the 1,2-dioxetanes, the presence of the $\overline{\mathrm{COOC}}$ conjugated ring, is responsible for their great sensitivity to temperature, substituents, and solvent [6], and one can assume, the change in the aggregational state of the solvent also affects their thermal stability.

EXPERIMENTAL

Tetramethyl-1,2-dioxetane (I) was synthesized by the method described in [7]. The benzene was treated with H_2SO_4, dried over $CaCl_2$, and distilled. Sulfolane (SL) was dried over 4 Å molecular sieves and distilled under vacuum. The scintillation-grade xylene was used without further purification. Solutions of tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)europium ($Eu(fod)_3$) were prepared by dissolving the required weights of the substance in o-xylene. All operatures were performed in a box, previously dried with P_2O_5, under dry argon.

Measurements of intensity, CL spectra, and quenching time of the luminescence (τ) were made on the setups described in [8, 9]. The photoluminescence spectra (PL) were recorded on a Hitachi MPF-4 spectrofluorometer.

RESULTS AND DISCUSSION

Thermolysis of compound (I) leads to the formation of electron-excited acetone in high yield (η = 30% [10]) and is accompanied by strong CL (reactions 1 and 2).

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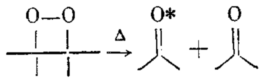
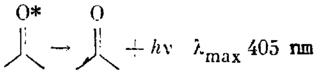
TABLE 1. Activation Parameters of the Thermal Decomposition of (I) in the Liquid and Crystalline Phases of Benzene and Sulfolane

Solvent	Sensitizer, mole/liter	E_a, kcal/mole	
		liquid	solid
Benzene	—	27.9±2,0	27,8±1,6
Sulfolane	—	29,9±1.5	19,9±1,8
	$Eu(NO_3)_3 \cdot 5H_2O$, $3 \cdot 10^{-2}$	28.1±1,2	23.0±0,9
	$Eu(fod)_3$, $1 \cdot 10^{-3}$	27,0±1,4	28,6±1,3



(1)



(2)

The activation energies (E_a) of the thermolysis of (I) in o-xylene as determined by us from the Arrhenius relationship was 27.4 ± 3.0 kcal/mole ($\Delta S^{\neq}$ = 2.2 ± 0.8 cal/mole·deg), close to the values of E_a obtained in other solvents [10, 11].

The combination of a high value of η and a relatively low value of E_a make it possible to monitor the kinetic decomposition of (I) by the CL over a broad temperature range.

When a solution of (I) (1.2 M) in SL (300-260 K) freezes, at the moment of the phase transition (278 K) a rise in the CL (I_{CL}) of compound (I) is observed against the background of monotonic decrease (Fig. 1). The increase in I_{CL}, as can be seen from Fig. 1, is not caused by the temperature rise resulting from the crystallization of the solution, but is perhaps due to the decomposition of (I) catalyzed by the change in the aggregational state of the solvent. The acceleration of the decomposition of (I) as the SL is converted to the solid phase is also indicated by a decrease in the activation energy (Table 1). The value of E_a is determined from the relationship ln I vs. 1/T. Corrections for the change in the luminescence yield of the acetone during freezing and the transparency of the solution after the phase transition were made on the basis of measurements of the temperature dependence of the intensity of the PL of the acetone.

In contrast to SL, the rise in I_{CL} during the phase transition of a solution of compound (I) (1.2 M) in benzene (Fig. 2) is due exclusively to the rise in the temperature during crystallization of the solvent. The determination of E_a showed that the formation of the crystal phase of benzene has no effect on the decomposition kinetics of (I) (Table 1).

Despite an abundance of examples of a sharp increase in the rate of reaction in freezing solvents [3], at the present time there is no commonly accepted view concerning the mechanism of these phenomena. For organic solvents, the idea that the reagents are concentrated in unfrozen regions is being investigated [4]. For reactions in ice, it has been suggested that the juvenile surface of the solid phase acts as a catalyst [5].

The decomposition of (I) is a unimolecular process, the rate of which does not depend on the concentration of the substance and its nonuniformity during freezing, which allows us to reject the hypothesis of catalysis as a result of the concentration of the starting reagents in unfrozen regions. On the other hand, comparing the data on the freezing of solution (I) in benzene and in SL, we see that the acceleration of the decomposition of (I) induced by the phase transition of the system also cannot be explained by the high physicochemical activity of a juvenile surface alone.

In our opinion, the most probable mechanism of the catalysis for the given system are structural changes in the molecular complex SL–(I) in the solid phase of the solvent. In the liquid phase the weak intermolecular interactions have no significant effect on the stability of (I). At the same time, the presence of earlier-formed complexes in the liquid phase after the phase transition may lead to a reorientation of the molecules that proves favorable to the decomposition of (I).

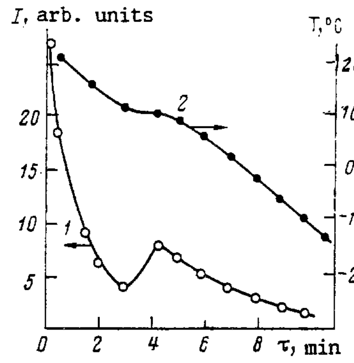


Fig. 1

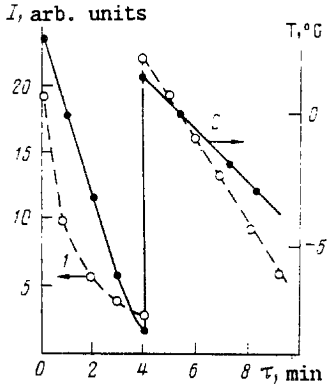


Fig. 2

Fig. 1. Temperature dependence of the intensity of the CL of the thermal decomposition of (I) (1.2 M) in sulfolane (1). Temperature change (2).

Fig. 2. Temperature dependence of the intensity of the CL of the thermal decomposition of (I) (1.2 M) in benzene (1), temperature change (2).

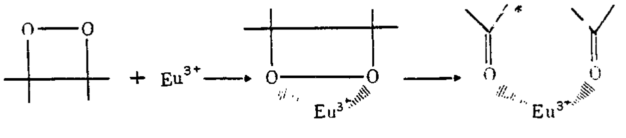
TABLE 2. Activation Parameters of the Thermal Decomposition of (I) in Xylene

Sensitizer, mole/liter	T, K	Rate constant $k\cdot10^5$, sec^{-1}	Activation energy, kcal/mole	$\Delta S^{\neq}$, cal/mole·deg
–	326	3.9±0.2	27,4±3,0	2,2±0,8
	337	13.2±0.3		
	348	38.1±0.3		
	357	153.0±8,0		
$Eu(fod)_3$ 10^{-2}	316	98±0,2	19,9±2,6	-11,8±2,6
	319	125±3.3		
	328	400±3,6		
	336	581±19,9		

Additional information in favor of this hypothesis was obtained in a study of the activation of CL of (I) by the sensitizer $Eu(fod)_3$.

It was found that introducing any third component to the system that reacted with (I) or with SL could eliminate the solid-phase catalysis, since in the formation of the complex of (I) it will be screened from interaction with solvent molecules and the phase transition will have less effect on its stability.

It was shown earlier in [12] for 1,2-dioxetane-9-(2-adamantylidene)-N-methylacridan and by us for diadamantylidene-1,2-dioxetane in [13] that $Eu(fod)_3$ is effective in catalyzing their decomposition. The catalytic effect is explained by the formation of a complex of Eu(III) with (I) (reaction 3).



(3)

For indicating the progress of the complex formation we used the kinetic luminescence spectroscopic method suggested in [14] that is based on the dependence of the length of time required for the CL to be extinguished (τ) on the immediate environment of the luminescing center. For example, adding diadamantylidene-1,2-dioxetane ($4\cdot10^{-4}$ M) extinguishes the PL of the Eu(III) ion, lowering its τ from 100 μsec in the absence of the extinguisher to 15 μsec.

Compound (I) has a similar effect on the lifetime of $Eu(fod)_3$ in the excited state, which points to the formation of a complex. In fact, from spectroscopic—kinetic experiments

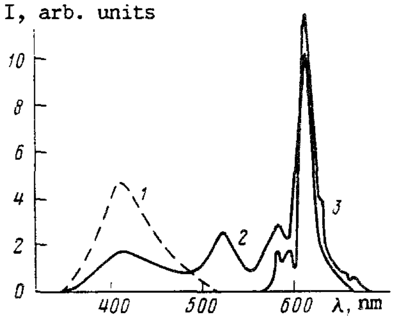


Fig. 3. Spectra: CL in the thermolysis of (I) (10^{-2} M, 323 K, xylene) (1), CL in the thermolysis of a solution of (I) (10^{-2} M) and $Eu(fod)_3$ (10^{-3} M) in xylene at 323 K (2), PL of $Eu(fod)_3$ (10^{-3} M, xylene, 298 K, $\Delta\lambda = 1$ nm) (3). The spectra (1, 2) were recored on an SSR-1 spectrometer with an FÉU-39 photomultiplier tube, $\Delta\lambda = 10$ nm.

it has been established that Eu(III) not only activates the CL of (I) (Fig. 3), but actually causes its decomposition to proceed hundreds of times more rapidly (Table 2).

The addition of $Eu(fod)_3$ to a solution of compound (I) in sulfolane, as was expected, results in the transition of the system in the process of cooling from the liquid to the solid phase not causing any change in the activation parameters of the decomposition of (I) (Table 1). It turned out, however, that no catalytic action was observed in the liquid phase of the SL, either. Measurements of $\tau Eu(fod)_3^*$ in the presence of SL showed that the latter interacts with Eu(III). The lack of catalytic activity by $Eu(fod)_3$ in the liquid phase SL is apparently caused by the complicated competing processes of interaction between Eu(III) and SL in the formation of the complex with (I). It should be noted that the elimination of the catalysis of the decomposition of (I) in solid phase SL on the addition of $Eu(fod)_3$ also provides grounds for rejecting the possibility of concentration in the unfrozen region of impurity molecules which can act as a catalyst.

From the foregoing it follows that adding an activator, when this is inert relative to complex formation with (I), should not have any effect on the catalysis of its decomposition by solid phase SL. The length of time required for the luminescence of europium nitrate to die out does not depend on the presence of (I). Thus, $Eu(NO_3)_3 \cdot 5H_2O$ does not enter into the reaction of the complexation with (I) and does not change the E_a of the decomposition of (I) in liquid or solid phase SL (Table 1).

The lowering of the temperature that leads to the freezing of the solvent may thus entail an acceleration of the decomposition of (I).

CONCLUSIONS

It has been established that the rate of decompostion of dioxetanes changes in in sulfolane solutions on transition from the liquid to the solid phase, which is explained in terms of structural changes of the molecular complexes dioxetane—sulfolane in the solid phase of the solvent.

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