THERMAL DECOMPOSITION OF 9,10-DIOXYANTHRACENE

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Kinetic characteristic and the course of thermal decomposition of 9,10-dioxyanthracene to a great extent depend upon the way of its isolation and upon the conditions of its thermal decomposition. At the decomposition in molten naphthalene all differences become compensated and therefore we ascribe them to different structural modifications formed due to different ways of crystallisation of anthracene photoperoxide. This fact can also explain such a large dissipation of melting point values of 9,10-dioxyanthracene, as much as 40°C, quoted in literature. Rate constant of decomposition of anthracene photoperoxide in molten naphthalene can be expressed as $k = 3$. $. 10^{14} \exp(-30000/RT)$ (s^{-1}). Heat of decomposition reaction is 55 ± 5 kcal/mol. Higher values of activation energy of decomposition of pure 9,10-dioxyanthracene or its mixtures with anthracene or aluminium oxide are explained by a contribution of activation energy of formation of reaction centers in solid matrix.

9,10-Dioxyanthracene, often called photoperoxide of anthracene, belongs to the class of transannular peroxides formed by photosensitised oxidation or by reaction of singlet oxygen with corresponding hydrocarbons[1,2]. Oxygen is fixed to a conjugated diene[2-5], by normal covalent bonds as a bridge. Behaviour of transannular peroxides at higher temperatures depends upon their structure. While some of them, *e.g.* 9,10-diphenyl-9,10-dioxyanthracene, decompose reversibly to give oxygen and the original hydrocarbon in almost 100% yield, others give lower yields of this reaction and photoperoxide of anthracene does not evolve any oxygen when heated[6]. Kinetic characteristics of 9,10-dioxyanthracene decomposition have so far been measured only indirectly — from the data of styrene polymerisation in the presence of photoperoxide[7]. But for the decomposition in solid state there are not available even such data; only a note that photoperoxide of anthracene decomposes below its melting point[8,9].

We have assumed that detailed study of this problem may explain controversial data about 9,10-dioxyanthracene and generally contribute to the knowledge of peroxide decomposition, mainly in solid state. Structural changes of decomposing crystalline 9,10-dioxyanthracene forming thus mixed crystals of anthraquinone and anthrone were followed by X-ray analysis[10]. In the study it was observed that mixed crystals are formed in two preferential orientations with respect to the orientation of the original monocrystal. Reaction products in these two preferential orientations are formed in unequal amounts which indicates different rates of decomposition of different structures.

EXPERIMENTAL

9,10-*Dioxyanthracene* (I) was prepared by photooxidation of anthracene in chloroform in the presence of methylene blue as sensitizer[10]. As the calorimetric measurements of decomposition

of *I* have shown that the course of decomposition reaction depends on the last stage of isolation, all measurements were performed both with *I* prepared by freezing out from carbon disulphide solution at $-25°C$ (*Ia*) and with *I* obtained by precipitation of benzene solution with light petroleum (*Ib*). Endotherm of melting could not be recorded, but the thermal stability of peroxides isolated by different procedures were also different. Large dissipation of melting point or decomposition temperature values quoted in literature: 120°C with decomposition[9], 139—143°C (ref.[11]) and 146—147°C (ref.[12]) without decomposition, 160°C or 166°C with explosive decomposition (ref.[8,10]), may be due to the same reason. The yield depending upon the purification method used varied from 20 to 30%. All measurements were done after the synthesis as soon as possible and samples of anthracene photoperoxide were stored in dark bottles in a refrigerator in order to avoid slow thermal decomposition at room temperature and by light. The presence of impurities, mainly of anthracene, anthrone and anthraquinone, was checked by sorption liquid chromatography in tetrahydrofurane–water (35 and 65 vol.%) and Corasil C-18 as solid phase. After repeated crystallisation from chloroform and freezing out from carbon disulphide or precipitation from benzene no impurities of the peroxide could be detected by the above mentioned method. Synthetised 9,10-dioxyanthracene was identified by IR spectroscopy, using KBr discs-technique, according to the following absorption bands: 1 460, 1 170, 1 950, 880, 770 and 720 cm^{-1} (ref.[10]) and by UV spectroscopy of dioxane solution $-\lambda_{max}$ 270 and 278 nm (ref.[12]). Thermal decomposition of anthracene photoperoxide was followed by a differential calorimeter Perkin-Elmer, Model DSC-1B, either isothermally or at linearly increasing temperature.

Isothermal measurements of anthracene peroxide decomposition in naphthalene were evaluated by following logarithm of the rate of reaction heat evolution (mcal s^{-1}) *vs* time. Isothermal decomposition in solid state was, with respect to autocatalytic decomposition, evaluated from the maximum rate of decomposition (v_{max}) and the time (τ_{max}) required to attain v_{max}. Rate constants from DEA curves were determined according to Barret's method[13] at given temperatures and assumed first order of the decomposition reaction. Kinetic parameters (energy of activation, frequency factor) were obtained from Arrhenius' equation and heat of reaction evolved at the decomposition of *I* by a graphical integration of areas under DEA curves or the curves of isotherms and appropriate recalculation.

RESULTS

Decomposition in Molten Naphthalene

Naphthalene was chosen as a solvent for measuring the decomposition of *I* because of the solubility of *I* in it, its high boiling point and the advantage of weighing the solid solvent directly into measuring capsules. Weighed samples were gas-tight closed, left for 1 min at 355 K (melting of naphthalene and dissolving of *I*) and then heated at a required temperature or at a linearly increasing temperature according to a selected programme.

Isothermal decomposition. Rate constants of all isothermal decompositions of *I* in naphthalene were calculated from the dependencies analogous to those depicted in Fig. 1 (Table I). Energy of activation of the isothermal decomposition of *I* in naphthalene was 30 kcal/mol and frequency factor $3 . 10^{14}$ s^{-1} irrespective of the way

of isolation of I and in a good agreement with the value quoted by Breitenbach[6] (29·8 kcal/mol). Regardless the shifted temperature range and the solvent choice the values of the rate constants lay on one straight line (Fig. 2).

Decomposition at programmed temperature increase. When plotting log k vs f. . $(1/T)$ it was found that these dependences are not linear within the given temperature range (Fig. 3) indicating thus that energy of activation is changing in the course of reaction. The value of activation energy 30 kcal/mol which holds for isothermal

TABLE I

Values of Rate Constants for Isothermal Decomposition of Anthracene Photoperoxides Isolated by Various Methods in Molten Naphthalene at Concentration of I of 1 mg per 5 mg of Naphthalene

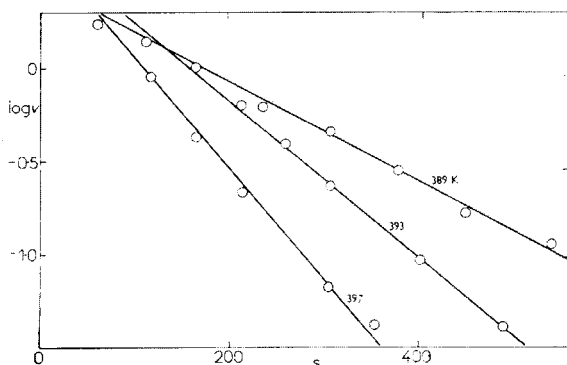| Ia		Ib	
T, K	$k \cdot 10^3$, s^{-1}	T, K	$k \cdot 10^3$ s^{-1}
375	1·6	378	2·4
382	4·2	388	4·1
389	6·2	393	10·5
393	10·2	403	22·0
397	13·8	413	78·0
401	22·5	—	—

FIG. 1

Logarithm of Rate of Reaction Heat Evolution at Decomposition of 9,10-Dioxyanthracene — Ia (1 mg) in Molten Naphthalene (5 mg) at Different Temperatures

conditions is in this case attained at the conversion of $25-60\%$. Besides this, the two extreme and largely different values of activation energy were obtained; one (E_1) at the conversion of $10-25\%$ and the other (E_2) at $70-90\%$. As the evaluation of results in the $0-10\%$ and $90-100\%$ conversion ranges is less accurate these ranges were not further considered, While E_1 depends on the concentration of I in naphthalene, E_2 is independent of it (Fig. 4). The value of E_2 attains only about 20 kcal/mol; this we can not simply and adequately explain. The higher value of activation energy for initial stages of decomposition and higher concentrations of I in naphthalene is evidently connected with its limited solubility and thus the decomposition partly proceeds in solid phase of nondissolved 9,10-dioxyanthracene and exhibits considerably higher energy of activation.
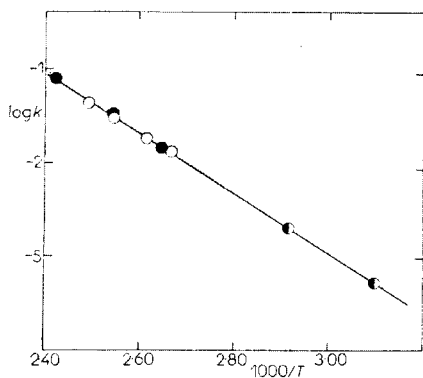

FIG. 2

Arrhenius' Plot of Rate Constants [s^{-1}] of 9,10-Dioxyanthracene Decomposition Determined from Isothermal Measurements in Naphthalene ($\circ$ *Ia*, $\bullet$ *Ib*) and from Rates of Styrene Polymerization ($\bullet$)[7]
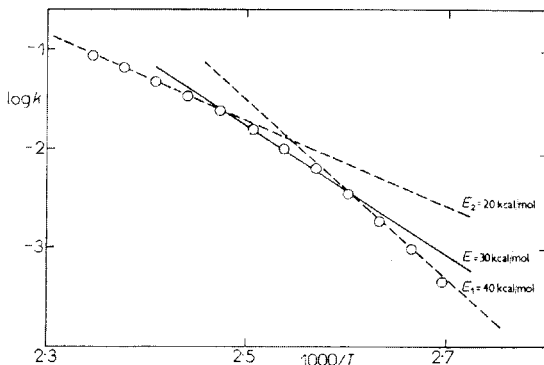

FIG. 3

Dependence of Logarithm of Rate Constants of 9,10-Dioxyanthracene Decomposition in Naphthalene on Reciprocal Value of T at Measurements with Programmed Temperature Increase 16°C min^{-1}; 10% of *Ia* in naphthalene.

Heat of decomposition of *I* in molten naphthalene at the rate of heating of 16°C min^{-1} is 55 ± 5 kcal/mol and is neither dependent on the preparation procedure of *I* nor the concentration of *I* in naphthalene. Small differences in the results are probably due to an inaccuracy of weighing or results evaluation. It is worth to note that the same values of reaction heat were obtained at isothermal decomposition of *I* in naphthalene.

Decomposition of I in Solid State

Isothermal decomposition. If *I* is heated in the $350-410$ K region an autocatalytic decomposition is observed. Isothermal curves, temperatures of maximum rates and also maximum rates of decomposition were found to be largely dependent upon the way of isolation of *I*. Most of them exhibit irregularities — two or even three exotherms. In all measurements the autocatalytic decomposition starts immediately when the samples are heated up and no induction period could be detected; the results indicate that in the crystal there are plenty of different defective centers.

Apparent effective energy of activation of isothermal decomposition of *I* in solid state calculated from maximum rates and time intervals which were needed for attaining the maximum rate is in the range of $25-35$ kcal/mol, irrespective of the way of isolation of *I* and despite the fact that the temperature of maximum rate of heat evolution at decomposition of *Ia* is as much as by 25°C lower than of the decomposition of *Ib*. A considerable dissipation of values of apparent energy of activation is due to a lowered reproducibility and difficulties in evaluation of isotherms having several exotherms.

Comparatively the most regular courses of isotherms were obtained if 10% mixture of *Ib* with Al_2O_3 and anthracene was tempered after careful mixing (5 min in a homogenizer). It is rather interesting to study the effect of the two admixtures on the decomposition of anthracene peroxide. Isotherms of mixtures with anthracene have no

TABLE II

Values of Apparent Activation Energy (in kcal/mol) for Isothermal Decomposition of *Ib* in Mixtures with Al_2O_3 and with Anthracene in Dependence on the Way of Evaluation (10% wt. of *Ib*)

Method	*Ib*-Anthracene	*Ib*-Al_2O_3
$\log v = f(t)^a$	27·5	27·5
$\log v_{max} = f(1/T)$	33·0	31·5
$\log (1/\tau_{max} = f(1/T)$	$-$ [b]	33·5

^{a} Declining part of the dependence. ^{b} As the isothems have no prominent maximum, τ_{max} is hard to define.

prominent maximum and simultaneously the maximum rates and the rate constants are 4 to 5-times lower than in case of mixture with aluminium oxide, but the values of apparent energy of activation for individual processes are about the same (Table II).

Decomposition of Ia *at programmed temperature increase.* At the rate of temperature increase of $4°C \min^{-1}$ the maximum reaction rate is attained in the temperature range of $386 - 390$ K; heat of reaction is 75 ± 5 kcal/mol and activation energy $50 - 55$ kcal/mol. The decomposition reaction proceeds probably without melting of *I* or its decomposition products, because the sample during decomposition turns from white to yellow-brown, but does not change its powder-like structure.

Different course of decomposition was observed when the rate of temperature increase was $8°C \min^{-1}$ or higher. Up to a certain stage, the reaction proceeds as in the previous case, but then the rate suddenly jumps up and the reaction becomes explosive. This is probably connected with an accumulation of reaction heat which could not be at an increased rate of heating removed and when the amount of heat attains a critical value the explosive decomposition takes place. The time of the whole reaction is only several seconds.

Heat of reaction is slightly lower than in case of the rate of $4°C \min^{-1}$ and attains the value of 60 ± 5 kcal/mol. The lower value of the heat of reaction is probably due to subsequent-endothermal reactions. Even if no endotherm of melting could be seen on the curves the red-brown, hard and glassy melt was observed after the reaction in standard Perkin-Elmer pans. Apparent energy of activation of the first stage of decomposition is 100 ± 20 kcal/mol and of the explosive part of about 500 kcal/mol.

TABLE III

Values of T_{max} (K), Apparent Activation Energy and Heat of Reaction (kcal/mol) for *Ia, Ic* and *Ib* at the Rate of Temperature Increase $4°C \min^{-1}$

Sample	T_{max}	E	$-\Delta H$
Ia	388	55	75
Ic	391	60	80
Ib	412	50 (140)[a]	55

[a] Lower value corresponds to conversion of decomposition of $10 - 30\%$; the value in brackets corresponds to the conversion of 70 to 90%.

TABLE IV

Values of T_{max} (K), Apparent Activation Energy and Reaction Heats (in kcal/mol) of *Ib* in Mixtures with Al_2O_3 in Dependence on Concentration

E_1 is valid for conversions $10 - 30\%$; E_2 is valid for conversions $70 - 90\%$.

% *Ib*	E_1	E_2	$-\Delta H$	T_{max}
100	48	140	55	412
80	64	170	55	413
50	63	210	52	413
20	75	300	51	412
10	63	180	45	399
7	60	100	40	392
5	60	90	40	389

Decomposition of Ib *at programmed temperature increase.* Comparable temperature of decomposition at the rate of temperature increase of 4°C min^{-1} shifts from 387 K obtained for *Ia* to 412 K. Apparent energy of activation increases and is independent of temperature. At low conversion $(10-30\%)$ it reaches the value of about 50 kcal/mol and at high conversions $(70-90\%)$ of about 140 kcal/mol. As the course of decomposition of *Ia* and *Ib* in molten naphthalene is identical, these differencies can be ascribed to different structural modifications formed by freezing out of *I* from carbon disulphide and by precipitation of benzene solution with light petroleum. In order to prove this assumption, *Ib* was frozen out from CS_2 *(Ic)* and decomposed under the conditions of programmed temperature increase of 4 and 8°C min^{-1} (Table III). The course of differential curves, heat of reaction, T_{max}, as well as kinetic parameters are very close to the values obtained for decomposition of *Ia*.

Another difference of decomposition of *Ib* in contrast to *Ia* is that at the heating rate of 8°C min^{-1} the reaction is not strictly explosive. The course of differential curves is irregular and badly reproducible. Strictly explosive character reaches the reaction at the rate of heating of 16°C min^{-1}. Energy of activation of the first part of decomposition is 80 and of the explosive part of about 400 kcal/mol.

Mixtures of 9,10-*dioxyanthracene with aluminium oxide and anthracene.* DEA curves of decomposition of mixtures *Ib* with Al_2O_3 were measured at different concentrations and different rates of heating. The first change in the course of decomposition curves, which was apparent without further evaluation, was higher sym-
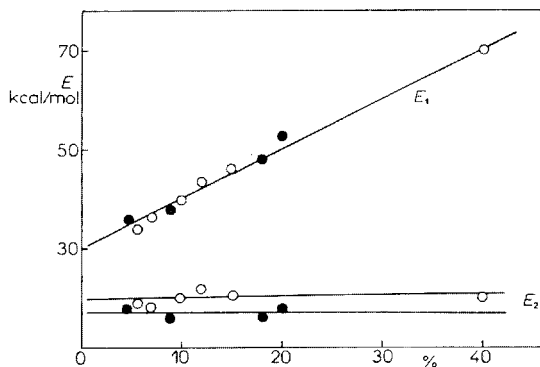

FIG. 4

Partial Activation Energies E_1 and E_2 (see Fig. 3) of Decomposition *vs* Concentration of 9,10-Dioxyanthracene in Naphthalene at Rate of Temperature Increase of 16°C min^{-1}

○ *Ia*, ● *Ib*, E_1 corresponds to the $10-30\%$ conversion and E_2 to $70-90\%$.

metry and an absence of irregularities when compared with the decomposition of pure *Ib*.

The values obtained of apparent activation energies, reaction heats and the temperature at maximum rate of decomposition in dependence on the concentration of *Ib* in the mixture, are given in Table IV. Again, the nonlinearity of the relationship $\log k = f(1/T)$ forced us to divide the interval into two parts with two apparent activation energies. The initial part gives the value of about 60 kcal/mol, while the the later stages of decomposition exhibit values from two- to five-times higher.

Another distinguished change is a nonexplosive course of decomposition of the mixture of 10% *Ib* in Al_2O_3 at the rate of heating of 16°C min^{-1}. The presence of Al_2O_3 supports better distribution of anthracene photoperoxide particles and simultaneously improves heat transfer and therefore the heat can not be accumulated as to "start-off" an explosive reaction. Even if the rate of heating is increased to 32 or 64°C min^{-1} the decomposition does not become explosive. The decomposition curves of mixtures of *Ib* with anthracene are more regular than those of pure *Ib*. But, what is more important, the activation energy of decomposition in the initial stage decreases with gradual dilution of *Ib* with anthracene and at low concentrations the same value is attained as in a liquid medium or at isothermal decomposition (Table V).

A very interesting course of decomposition is observed if *Ia* is mixed with anthracene. Not only the comparable temperature of decomposition is increased by about 10°C but the addition of anthracene causes also the formation of two maxima. Besides that, also the explosive course of reaction is suppressed even at the rate of heating of 16°C min^{-1}. Therefore the addition of anthracene somehow stabilizes 9,10-dioxyanthracene. The temperature range widens and the energy of activation decreases ($E = 30$ kcal/mol).

TABLE V
Values of T_{max} (K), Apparent Activation Energy and Reaction Heat (kcal/mol) of Decomposition of *Ib* in Mixtures with Anthracene in Dependence on Concentration
Rate of temperature increase: 4°C min^{-1}. E_1 holds for conversions of 10—30%; E_2 holds for conversions of 70—90%.

% *Ib*	E_1	E_2	$-\Delta H$	T_{max}
100	48	140	56	412
80	41	130	55	412
50	43	145	55	412
20	35	125	60	412
10	30	145	60	413

DISCUSSION

Decomposition of 9,10-dioxyanthracene in liquid medium proceeds with energy of activation 30 kcal/mol. Activation energy in solid state is ambiguous. The ambiguity, which requires further discussion, lays in the fact that while at isothermal measurements even in solid state we obtain the value of activation energy which is comparable with the data of decomposition in molten naphthalene, but under the conditions of programmed temperature increase the activation energy decomposition markedly increases. For the initial stage of decomposition of pure 9,10-dioxyanthracene (irrespective of the way of crystallization) as well as for its mixture with aluminium oxide, the energy of activation is 55 kcal/mol. The value of 30 kcal/mol was obtained only if 9,10-dioxyanthracene was diluted with anthracene. Even if anthracene during decomposition is neither in liquid form not liquifies 9,10-dioxyanthracene, its presence manifests itself as if 9,10-dioxyanthracene were dissolved in naphthalene. From this fact we can draw the conclusion that the decomposition of 9,10-dioxyanthracene proceeding as a result of the presence of defects in crystal lattice has the same activation energy as the decomposition in solution. Then if 9,10-dioxyanthracene contains enough defective centers or if the rate of formation of defective centers at given temperature is higher than the rate of decomposition in these defects of the crystal lattice then activation energy of the initial stage of decomposition will be 30 kcal/mol. And, on the contrary, if the development of the decomposition reaction in solid phase is limited by the formation of reaction centers then also the activation energy of decomposition will be determined by the slowest process. If we imagine that the formation of defective centres is determined by the diffusion of anthracene molecules, (or anthracene photoperoxide) then the decomposition should proceed with the same energy of activation. Here, we can note, that very similar value was quoted for activation energy of diffusion of anthracene molecules in anthracene, *i.e.* 56 kcal/mol (ref.[14]).

The formation of a reaction center can also be due to a spontaneous decomposition of several molecules of 9,10-dioxyanthracene in the crystal lattice. However, such a process requires as many times higher activation energy of the fundamental process as many molecules in closed vicinity have to decompose at the same time in order to form an active reaction center[15]. Then the activation energy of the first stage of decomposition can be explained by the formation of reaction centers by a simultaneous decomposition of two neighbouring molecules of 9,10-dioxyanthracene. Analogously can be derived also higher values of activation energies of decomposition at higher temperature or at later stages of decomposition.

Now, let's stop at the problem of the explosive course of decomposition. In the preceding part we have satisfied ourselves with simple explanation of this phenomenon by overheating of the sample. If this explanation is a correct one then we have a problem how to explain different heating-up at the decomposition of photoperoxide

samples crystallized from different media. It seems that if the explosive decomposition would be due to an overheating then the overheating should be similar for both samples studied.

An alternative explanation of the explosive course of reaction can be based on the assumption that the probability of reaction centers formation does not depend only on temperature but also on physical structure of the compound being decomposed. If reaction centers are formed *via* excitation mechanism, then the probability of their formation is increasing also with dimensions of the crystallinic region which can energetically participate on the formation of the reaction center due to a simultaneous decomposition of molecules being in neighbourhood. This approach allows us to explain also the effect of admixtures on the decomposition of 9,10-dioxyanthracene. On one hand an added and homogenized aluminium oxide divides crystals of 9,10-dioxyanthracene and on the other separates them from mutual interaction and thus limits the formation of reaction centers.

To a crystalline medium, besides the possibility of collective excitation, we have to ascribe also the ability of collective dissipation of certain energetical levels. In this way we think that we can explain the shift of comparable decomposition temperature of *Ia* towards higher temperature in the presence of anthracene as well as the effect of this admixture on the isothermal decomposition.

Finally, we can not rule out that some of the observed phenomena at the decomposition of 9,10-dioxyanthracene in solid state can be connected with different gradients at different experiments. This aspect can become important if we admit that the decomposition of 9,10-dioxyanthracene depends upon orientation of the molecule in the crystal lattice and that crystalline 9,10-dioxyanthracene (or anthracene) has in the region studied characteristics of liquid (plastic) crystal. These compounds are known for their ability of orientation in the direction of the temperature gradient[16].

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