Phase equilibriums in the photocondensation of anthracene

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Experimental data are obtained on the phase equilibrium boundaries between anthracene and dianthracene crystals, on the one hand, and their molten mixture, on the other, as functions of the intensity of the applied ultraviolet radiation. The phase boundaries are calculated on the basis of the concept of a psuedobinary monomor-dimer system.

PACS numbers: 64.70.Dv, 64.70.Kb, 81.10.Bk

It was reported earlier[1] that application of light ($\lambda = 365$ nm) gives rise to production of photomodification (PM) crystals and liquid drops from initially unsaturated anthracene vapor. However, the nature of the photocondensate remained unclear. Our x-ray structure analysis of the PM single crystal grown from vapor at 520 K and cooled in a light beam of intensity $I = 10^{18}$ photons/cm² sec has made it possible to establish that this crystal has the usual orthorhombic lattice of dianthracene. Optical investigations have confirmed that it does actually consist of the molecules of the anthracene dimer. There data offer evidence that the monomer-dimer photochemical reaction is an attribute of light-induced phase transitions in anthracene. A similar change in the elementary components accompanies a large number of phase transitions, such as the isomorphic transition in cerium ($Ce^{3+} \rightarrow Ce^{4+}$), condensation of mercury (atom→electron + ion), etc. Anthracene is a most convenient model system for the investigation of the relation of phase transitions to processes in which the elementary components are changed.

In the present study we investigated transitions that are induced by light in condensed phases.

We have established that the already known[2] process of recrystallization of anthracene (A) into dianthracene (D) sets in at a certain threshold intensity $I_{thr} = I_{thr}(T)$.

Melting of anthracene, accompanied by precipitation of PM crystals was observed in Ref. 1 at $T = 413$ K and $I \approx 10^{19}$ photons/cm² sec. The dependence of the temperature of this type of melting (T_A^m) on I, which was investigated by us by thermomicroanalysis in an argon atmosphere, is illustrated in Fig. 1, which shows also the I-dependence of the melting temperature of the photomodification (T_D^m). These temperatures coincide with the triple vapor–liquid–crystal equilibrium and were determined by the same method as in Ref. 1.

The results can be described quantitatively on the basis of the theory of solutions.[1] The reversible growth observed by us in the extinction of thin layers of the melt and of the PM in the absorption bands of the anthracene ($\lambda = 405$ nm and $\lambda = 365$ nm) points to the presence of mixing of the monomer and dimer molecules in the liquid and

in the PM. When the PM crystals are extracted out of the exciting light beam and are subsequently abruptly cooled, the dimers are apparently monomerized practically completely into "sandwich" pairs that have at $T = 77$ K intense excimer-luminescence bands with $\lambda_m = 475$ nm and $\lambda_m = 580$ nm.[2] Although the PM crystals become cracked, their structure remains quite close to the crystal structure of the dianthracene.
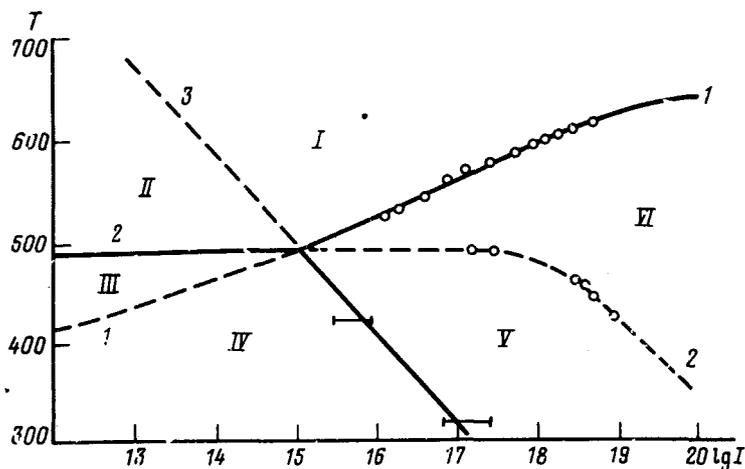

FIG. 1. Phase-equilibrium temperatures in the anthracene-dianthracene system vs the radiation intensity. Equilibrium lines: 1) $(L–D)$, 2) $(L–A)$, 3–$(A–D)$. The phase stability in regions I–VI is determined by the following sequence: I–ADL, II–DAL, III–DLA, IV–LDA, V–LAD, VI–ALD (the stability increases from left to right. The circles and the horizontal bars represent experimental data.

The concentration of the light-excited anthracene molecules (C_{A*}) can be described by the usual relation $C_{A*} = K_I I C_A$. The effective-mass law for the reaction $A + A^* = D$ leads to

$$C_D = K_2 C_A C_{A*} \exp(u/RT) = B_0 \exp(u/RT) I C_A^2 = BI C_A^2.$$ (1)

Recognizing that $C_A + C_{A*} + C_D = 1$ and that an estimate shows that $C_{A*} \sim 10^{-5}$ at maximum I, we have:

$$C_A = 1 - C_D = -\frac{1}{2BI} + \sqrt{\left(\frac{1}{2BI}\right)^2 + \frac{1}{BI}}.$$ (2)

Under conditions close to the $L–D$ phase equilibrium ($T = 550$ K, $I = 10^{18}$ photons/cm² sec) the dimer concentration C_D is estimated at ~ 0.01 in the melt and at ~ 0.997 in the PM. Taking into account the rather complete dimerization of the PM crystals, we neglect the solubility of the monomers in the the PM. Experiment has shown that dimers are not soluble in A. Thus, we can confine ourselves to the equilibrium between the liquid solution and pure anthracene and dianthracene crystals. This equilibrium is described by the equations

$$\Delta E_A = E_A^L - E_A^{cr} = T_A^0 \, \Delta S_A + R T \ln C_A(I,T), \tag{3a}$$

$$\Delta E_D = E_D^L - E_D^{cr} = T_D^0 \Delta S_D + R T \ln C_A(I,T). \tag{3b}$$

Here E is the energy, T_A^0 and T_D^0 are the melting points of pure anthracene and dianthracene.[3] The melting entropies ΔS_A and ΔS_D are assumed for simplicity to be independent of T and I. The use of Eqs. (3a) and (3b) corresponding to the ideal solution is justified by the fact that in the investigated range of I the dimer concentration in the liquid is low. In Eq. (3), the concentrations C_A and C_D are determined by relations (1) and (2), which follow from the condition that the free energy be minimal with respect to concentration. Therefore Eqs. (3) can be readily shown to be equivalent to equality of the free energies of the liquid and solid phases.

Starting from the condition of the best fit of the experimental function $T_A^m(I)$ to relation (3a), we obtained, using a special computer program, the effective kinetic coefficient $B_0 = (7.3 \pm 3) \times 10^{-22}$ cm^2 sec/photon and the effective activation energy 5.4 ± 2 kcal/mole. We chose for T_A^0 and ΔS_A the values 490 K and 14 cal/mole-deg, respectively. B_0 and u, estimated from the published data, are of the same order of magnitude.

Using these data and the experimental $T_D^m(I)$ dependence we used (3b) to estimate, with the same computer program, the values $T_D^0 = 650 \pm 5$ K and $S_D = 50 \pm 5$ cal/mole-deg. Relations (2) and (3) were used to plot the $A \rightarrow L$ and $D \rightarrow L$ phase-equilibrium temperatures against $\log I$. The line 3 in Fig. 1 was tentatively assumed to be straight.

Curves 1, 2, and 3 divide the (T–$\log I$) diagram into six single-phase region with different relative phase stabilities. Figure 1 explains the experimentally observed threshold for the $A \rightarrow D$ transition, the transition sequence $A \rightarrow L \rightarrow D$ in region VI, and also why illumination of a strongly supercooled anthracene melt (region V) causes initially the anthracene to crystallize[4] into the ordinary monoclinic modification of anthracene, which then goes over gradually into dianthracene.

The instability of the diathracene crystals is due to the instability of the dimer molecules. When these molecules are stabilized by irradiation, the energy of the Van der Waals interaction between them is sufficient to stabilize the dianthracene crystal.

The results obtained with the anthracene-dianthracene model system can be useful also to solve other problems, such as the production of metallic hydrogen. The instability of the hydrogen metallic crystals and liquid is due to the fact that association of their constituent parts (electrons and protons) into H_2 molecules is energywise highly favored. If this association is prevented by using some external action, say irradiation, then the energy of the metallic bond should be sufficient to stabilize the metallic hydrogen.

[1] This formulation of the problem came about as a result of a discussion and intepretation of the experimental results at Prof. V.L. Broude's seminar at the Institute of Solid State Physics of the USSR Academy of Sciences (Chernogolovka).

[2] Similar radiation of "Sandwich" pairs was investigated in Ref. 3.

[3] At T_D^0 the dianthracene melts into a liquid that consists only of dimers.

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