MECHANOCHROMATIC EFFECT AND THE FORMATION OF FREE RADICALS IN BIS(PHENYLPHTHALOYL)ETHANE DIMERS UPON MECHANICAL DESTRUCTION IN THE SOLID PHASE

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Phenylphthaloylmethane and its derivatives are oxidized to form dimers which are symmetri cal relative to the central C-C bond [1-4]. In the present work, we discovered the mechanochromic properties of dimers due to the formation of free radicals upon mechanical action on crystals of these compounds. Dimers containing a p-dimethylamino group in the phenyl substituent and various substituents in the phthaloyl ring were studied

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unsubstituted (a), 4-C1 (b), 5-C1 (c), 5-Br (d), 5-I (e), 5-NMe, (f), and 4,7-di-Ph (g).

In previous work [5-7], we showed that these compounds in organic solvents form an equilibrium system as a consequence of their reversible thermal decomposition to free radicals:  $\Phi - \Phi \xrightarrow[k_{-1}]{k_{-1}} 2\Phi$ , where  $k_1$  and  $k_{-1}$  are the rate constants for decomposition of the dimer and recombination of the radicals formed. Radicals  $\Phi \cdot$  (a)-(g) have strong absorption in the visible region (430-435, 650-660, and 700-725 nm, log  $\varepsilon = 4.1-4.3$ ). Thus, solutions of these dimers have thermochromic properties: they turn green upon heating but this color disappears upon cooling [5, 6].

Fine-crystalline powders of  $\Phi$ - $\Phi$  (a)-(g) upon trituration in a mortar, pressing in KBr pellets (for recording IR spectra), and dispersion in a ball mill also turn green. This color is characteristic for  $\Phi$ · free radicals and is retained for a long time.

The formation of free radicals upon the mechanical destruction of the dimer crystals was studied in detail by ESR spectroscopy for the  $\Phi$ - $\Phi$  dimer (a), which is a yellow crystalline powder in the initial state containing  $3 \cdot 10^{-5}$  mole/kg  $\Phi$ · free radicals (a), which is about  $1.6 \cdot 10^{-3}$  mole %. The ESR spectrum at ~20°C is a symmetrical singlet with ~17 Oe halfwidth.

The radical concentration in the dispersed samples of  $\Phi - \Phi$  (a) increases by hundreds of times relative to the starting state and then, decreases over time at temperatures above 273 K (Fig. 1, curve 1). The pattern of the kinetic curve for the decrease in concentration is typical for reactions in solid matrices: the rate of the process decreases strongly after annihilation of a portion of the free radicals (stepwise kinetics [8]). The kinetic curve is linear when plotted as  $[\Phi \cdot]/[\Phi \cdot]_0$  vs. log t (Fig. 1, curve 2). This behavior indicates a distribution of free radicals relative to the rate constants for their annihilation, which, in turn, is a result of physical nonuniformity of the sample. The form of the thawing curve (Fig. 2) shows that the distribution of the reagent species over activation energy is rather close to linear [8]. The mean effective activation energy for the free radical annihilation evaluated relative to the temperature dependence of the recombination rate at 25-55°C is about 70 kJ/mole.

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Fig. 1. Kinetic curve for the annihilation of 2-(p-dimethylaminophenyl)indane-1,3-dion-2-yl free radicals ( $\phi$ · (a)) in the dispersed solid dimer of these radicals  $\phi$ - $\phi$  (a) at 55°C (1) and its transformation (2). The initial radical concentration was 2.6·10<sup>-3</sup> mole/kg. The dispersion temperature was 20°C.

Fig. 2. The temperature dependence of the relative concentration  $[\Phi \cdot ]/[\Phi \cdot ]_0$  upon the maintenance of the dispersed sample for 5 min at each temperature.

The concentration of  $\Phi$  free radicals (a) hardly increases upon the action of hydrostatic pressure up to 2000 atm on solid samples of the  $\Phi$ - $\Phi$  dimer (a). Thus, shear deformation of the crystals is a condition for radical formation.

As indicated above, a thermochromic effect is characteristic for the dimers in solution. In contrast, a change in the free radical concentration is not observed upon heating of crystals of  $\Phi - \Phi$  dimer (a) up to 150°C. The color of crystals of  $\Phi - \Phi$  dimers (a)-(g) also does not change up to their melting points (> 200°C, decomposition). The lack of an increase in the radical concentration upon heating of the solid samples is apparently a consequence of the cage effect, that is, the highly hindered diffusion of radicals formed upon decomposition of the dimer molecules such that they cannot exit into the bulk and geminal recombination of the pair occurs.

Thus, the relatively high stability of  $\Phi$  radicals in dispersed solid samples of the dimer is a consequence of the circumstance that the radicals formed in a pair upon a given mechanical action are significantly removed from each other, while the molecular mobility of the species in the solid phase is very low. The radical concentration in the starting samples of  $\Phi$ - $\Phi$  dimers (a)-(g) is a function of the means of their generation and precipitation from the solvent.

The rate constant of the recombination of  $\Phi$  radicals (a)-(g) in the liquid phase  $k_{-1} \simeq 10^9$  liters/mole sec, that is, the recombination occurs almost upon each encounter with activation energy close to zero. Thus, the "superequilibrium" radicals in the dispersed samples of solid  $\Phi$ - $\Phi$  (a) are very rapidly annihilated upon the addition of small amounts of benzene and even in solvent vapors.

The recombination of  $\Phi$  radicals (a)-(g) in the liquid phase in hydrocarbon solvents is not accompanied by side reactions and this process is entirely reversible at 20-90°C. This is also presumably true in the solid phase. The simplicity of the radical transformations of the dimers hold some promise for their use as a convenient model for the study of diffusioncontrolled reactions and the cage effect in solid matrices.

The stability of 2-(p-dimethylaminophenyl)indane-1,3-dion-2-yl radicals  $(\Phi \cdot)$  is largely a function of the presence of the amino group in the phenyl ring, apparently due to charge transfer. The analogous dimer, bis(phenylphthaloyl)ethane which does not have such a group has greater thermal stability [9]. This compound does not have a dimer-radical equilibrium or mechanochromic properties in the solid phase.

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## CONCLUSIONS

1. Dimers in the bis(p-dimethylaminophenylphthaloyl)ethane series have mechanochromic properties due to the formation of free radicals upon mechanical action on the dimers in the solid phase.

2. The recombination of 2-(p-dimethylaminophenyl)indane-1,3-dion-2-yl radicals stabilized in the solid phase is stepwise in nature.

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