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INFLUENCE OF ONIUM SUBSTITUENT IN PHTHALOYL RING ON THERMODYNAMIC

PARAMETERS OF EQUILIBRIUM BETWEEN DIMER AND FREE RADICALS OF

2-(4-DIMETHYLAMINOPHENYL)-1,3-INDANDIONES

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2.2'-Bis[2-(4-dimethylaminophenyl)-5-trimethylammonio-1,3-indandione] diperchlorate and 2,2'-bis[2-(4-dimethylaminophenyl)-5-(2,4,6-triphenylpyridinio)-1,3-indandione] diperchlorate have very definite thermochromic and mechanochromic properties, owing to reversible dissociation into free radicals. The rupture energy of the central bond C^2-C^2 ' in 5-substituted 2,2'-bis[2-(4dimethylaminophenyl)-1,3-indandiones] in acetonitrile is 63-75 kJ/mole; in the dimer with the bulky 5-(2,4,6-triphenylpyridinium) substituent, the rupture energy is 51 kJ/mole. The equilibrium constants follow the Hammett equation ($\rho = 1.53$, acetonitrile, 293 K). Radicals with onium substituents are thermodynamically the most stable of the arylindandionyl radicals that are thus far known, owing to the significant contribution of electrostatic interactions.

In [1] we reported results from a detailed investigation of the equilibrium between dimer and free arylindandionyl radicals containing various uncharged substituents in the indane fragment. However, it appears that the presence of an onium substituent would stabilize the cation radical, not only because of electron-acceptor properties, but also because of Coulomb repulsion of the radicals. The repulsion effect of polychloro-substituted arylindandionyl radicals was evaluated in [2] by quantum-chemical calculations.

Arylindandiones and the corresponding dimers containing ammonium substituents were synthesized recently [3, 4], and this opened up the possibility of studying the influence of

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an onium substituent on the stability of the radical formed by thermal dissociation of the dimer



Since compounds (If) and (Ig) are soluble only in polar media, we used acetonitrile as the solvent in investigating the influence of substituents on the thermodynamic parameters of the equilibrium (1). The dimers (Ia-g) are of interest because of their strong inhibiting effect in reactions of low-temperature oxidation of aromatic hydrocarbons [5], and also because of their thermochromic, photochromic, and mechanochromic properties [1, 6, 7] and the possibility of their use as photoresistors in vacuum photolithographic processes [8].

Since the length of the central bond that is ruptured in the dimer (Ia) is 1.569 Å [9], i.e., practically no different from an ordinary single σ -bond (1.54 Å), the ease of decomposition of the dimers (Ia-g) into radicals is due to the relatively low bond energy, determined by delocalization of the unpaired electron through the system of conjugated bonds in the radical, and hence by the low spin density on the central C atom.

The kinetically unstable radicals (II) have high rate constants of recombination $(k_{-1}) \sim 10^9$ liters/(mole·sec), with a zero activation energy (ΔH_{-1}^{\neq}) [6].

EXPERIMENTAL

The equilibrium (1) was studied in MeCN, purified by distillation over potassium carbonate and then P_2O_5 . The EPR spectra were registered in sealed ampuls in a Varian E-104 RF spectrometer. The error in determining the concentration of radicals was $\leq 10\%$. The temperature of the samples in the resonator was held to within ± 0.1 K. The equilibrium constant (K) was calculated from the formula

$$K = k_1/k_{-1} = [(II)]^2/[(I)]_0 - 0.5[(II)]$$
(2)

IR spectra were obtained in a Specord M-80 spectrometer in KBr tablets and in solution in CD₃CN.

TABLE 1. EAS of Radicals (IIa-g) (348 K)

Radical	Solvent	λ_{\max} , nm (and log ϵ)			
(IIa) (IIb) (IIb) (IIc) (IId) (IIe) (IIf) (IIg)	C ₆ H ₆ C ₆ H ₆ MeCN C ₆ H ₆ C ₆ H ₆ C ₆ H ₆ MeCN MeCN	$\begin{array}{c} 430 (4.22) \\ 435 (4.26) \\ 440 (4.26) \\ 440 (4.24) \\ 440 (4.42) \\ 434 (4.36) \\ 447 (4.28) \\ 450 (4.27) \end{array}$	$\begin{array}{c} 650(4,04)\\ 660(4,07)\\ 663(4,07)\\ 660(4,05)\\ 660(4,18)\\ 625(3,86)\\ 670(4,13)\\ 670(4,15)\end{array}$	$\begin{array}{c} 704(4,15)\\ 715(4,20)\\ 733(4,20)\\ 720(4,15)\\ 720(4,31)\\ 770(4,01)\\ 740(4,30)\\ 740(4,33)\end{array}$	

Electronic absorption spectra (EAS) were recorded in a Beckman DU-7 spectrophotometer in a specially designed quartz cuvette. The temperature was held to within ± 0.1 K by an external liquid thermostat. In calculating the equilibrium constant (K), allowance was made for the change in solvent density with temperature. Values of K, ΔH° , and ΔS° of the equilibrium, and also the extinction coefficients (ϵ), were calculated from the experimental data by the least squares method.

In accordance with Eq. (2), we have the following relationship for the optical density due to the radicals (II)

$$[(I)]_0/D = D/K\varepsilon^2 l^2 + 1/2\varepsilon l \tag{3}$$

where $[(I)]_0$ is the initial concentration of the dimer (I); D is the optical density at the absorption maximum of (II) (733-740 nm, Fig. 1); ℓ is the length of the cuvette.

All of the changes in the EPR and EAS of solutions of (Ia-g) are reversible in the interval 293-363 K.

RESULTS AND DISCUSSION

The dimer (If), which contains the strong electron-accepting 5-trimethylammonium substituent, is obtained from the synthesis in the form of yellowish brown crystals, which darken upon storage in air. Recrystallization gives crystals that are very nearly black. A similar phenomenon was observed previously for 2,2'-bis[2-(4-dimethylaminophenyl)-4,5,6,7tetrachloro-1,3-indandione] (Ih) and 2,2'-bis[2-(4-dimethylaminophenyl)-5-cyano-1,3-indandione] (Ii) [10]. The black color and the sharp decrease in solubility in comparison with the yellow modifications indicate structural changes of the crystalline state [generation of free radicals (II), complexation].

In the IR spectrum (KBr) of the black modification of the dimer (If) in the region of vibrations of multiple bonds 1800-1500 cm⁻¹, two low-intensity absorption bands of carbonyl groups are found at 1743 cm⁻¹ (ν_s) and 1712 cm⁻¹ (ν_{as}), and also bands at 1666, 1636, 1608, 1582, 1540, and 1520 cm⁻¹ due to stretching vibrations of C····C bonds of the aromatic rings and also vibrations of C····C and C····C bonds of the black forms. The IR spectra are similar for the black modifications of the dimers (Ih) and (Ii), which also consist of mixtures of the normal dimer (I) and a deeply colored phase.

In the crystalline state of the black modification of the dimer (If), free radicals have been detected. The EPR spectrum of the radical (IIf) at 293 K is a symmetric singlet with a half-width ~15 G (g = 2.0036). The degree of dissociation of the dimer, defined by the expression $\alpha = [(II)]/2[(I)]_0$, is small, amounting to only 1.05%.

The large volume of the 2,4,6-triphenylpyridinium substituent is apparently the reason it is impossible to form the dimer (Ig) of the deeply colored phase, so that we were able to isolate only the stable yellow form. The IR spectrum of the dimer (Ig) in KBr contains characteristic bands of stretching vibrations of carbonyl groups (1742 and 1713 cm⁻¹) and also bands of stretching vibrations of aromatic rings at 1620, 1605, 1597, 1551, and 1519 cm⁻¹; this is characteristic for all of the yellow modifications of the dimers [10]. The dimer (Ig) in the crystalline state also contains a small quantity of radicals ($\alpha = 0.42\%$). The EPR spectrum at 293 K is a singlet with a half-width ~22 G (g = 2.0036).

The dimer (Ia) is characterized by a very small content of free radicals, $\alpha = 3.2 \cdot 10^{-3}$ % (293 K).



Fig. 2. Dependence of $[(I)]_0/D$ on D in acetonitrile ($\ell = 3.1$ cm) at the following temperatures (T, K) and dimer concentrations (×10⁵ M; change in concentration in the series corresponds to positions of points from left to right): 1) (Ib), 347 (12.1; 10.3; 8.5; 6.0; 3.6; 1.2); 2) (If), 320 (3.73; 3.06; 2.19; 1.31; 0.87; 0.44); 3) (If), 327 (4.08; 2.78; 1.85; 1.32; 0.93; 0.68; 0.40; 0.31; 0.20); 4) (If), 343 (2.72; 1.80; 1.29; 0.90; 0.68; 0.40; 0.30; 0.19); 5) (Ig); 324 (2.94; 2.42; 1.73; 1.03; 0.69; 0.35; 0.17); 6) (Ig), 340 (3.39; 2.88; 2.37; 1.70; 1.01; 0.68; 0.34; 0.17).

Fig. 3. Temperature dependence of equilibrium constant on the basis of EAS data with the following concentrations of dimers, M: 1) (Ie), 1.61 \cdot 10⁻³; 2) (Ia), 2.6 \cdot 10⁻³; 3) (Id), 2.17 \cdot 10⁻⁴; 5) (Ic), 4.18 \cdot 10⁻⁴; 6) (If), 3.35 \cdot 10⁻³ (according to EPR data); 7) (If), 1.82 \cdot 10⁻⁵; 8) (Ig), 1.81 \cdot 10⁻⁵; 4) (Ib), 1.21 \cdot 10⁻³ (ℓ = 3.1 cm, acetonitrile).

Solvent	Dielectric constant, 293 K	λ_{max} , nm				
		(IIa)	(IIb)	(IIc)	(IId)	
C ₆ H ₆ MeCN	2,28 37,50	$647, 716 \\ 659, 730$	650, 715 664, 737	660, 720 664, 738	660. 720 666, 738	

TABLE 2. Influence of Solvent Polarity on Long-Wave Region of EAS of Radicals (IIa-d) (293 K)

When the black dimer (If) is ground in an agate mortar, the powder turns slightly green; there is a small increase in the concentration of free radicals as determined by EPR ($\alpha = 2-3\%$). The same treatment of the yellow dimer (Ig) leads to the formation of a dark green powder with a considerable content of free radicals ($\alpha = 20-30\%$). The mechanochromy of the dimer (Ia) [7], due to the increase in concentration of free radicals upon grinding the dimer in a mortar, is less than 1%.

In solutions of the dimers (If) and (Ig), we find far smaller differences than in the crystalline phase. The IR spectra of (If) and (Ig) in solution in CD_3CN have the characteristic vibrations of the yellow forms of the dimers: 1742, 1712, 1606, and 1520 cm⁻¹ (If); and 1742, 1713, 1623, 1606, 1600, 1552, and 1521 cm⁻¹ (Ig). Thus, the IR spectra of the dimer (Ig) in a KBr tablet is identical to that in CD_3CN solution. When the black dimer



Fig. 4. Dependence of $\triangle \log K$ on $\Sigma\sigma^{\circ}$ (a) and on $\Sigma\sigma$ (b) for dimer/free radical equilibrium system in acetonitrile (293 K): 1) NMe₂; 2) H; 3) I; 4) Cl; 5) Br; 6) NMe₃; 7) $\Sigma\sigma_{cor}^{\circ}$ for + NMe₃ group.

TABLE 3. Thermodynamic Parameters of Equilibrium (1) (Acetonitrile, 293 K)

Dimer	ΔH ⁰ , kJ/mole	∆S ⁰ , J/(mole• K)	ΔG ⁰ , kJ/mole	K, moles/liter
(Ia) (Ib) (Ic) (Id) (Ie) (If) (If) (EPR) (Ig) Error, %	73 65 65 63 75 66 66 51 ± 2	$\begin{vmatrix} 88\\ 83\\ 87\\ 74\\ 75\\ 119\\ 114\\ 71\\ \pm 6 \end{vmatrix}$	$\begin{array}{c} 46.9\\ 41.0\\ 39.4\\ 41.0\\ 53.4\\ 31.5\\ 32.0\\ 29.7\\ \pm 5\end{array}$	$\begin{array}{r} 4,4\cdot10^{-9} \\ 4,9\cdot10^{-8} \\ 9,5\cdot10^{-8} \\ 5,0\cdot10^{-8} \\ 3,0\cdot10^{-10} \\ 2,4\cdot10^{-6} \\ 2,0\cdot10^{-6} \\ 5,1\cdot10^{-6} \\ \pm 10 \end{array}$

(If) is dissolved in MeCN, a molecular solution is formed; therefore, the bands at 1666, 1636, 1582, and 1540 cm^{-1} , which are absent in solution, must pertain to vibrations of the deeply colored phase, the nature of which is not yet clear.

The EAS of the dimers (If) and (Ig) in the long-wave region have a single intense absorption maximum at 375 nm (If) and 390 nm (Ig) with extinction coefficients $\varepsilon_{375} = 1.8 \cdot 10^4$ and $\varepsilon_{390} = 1.2 \cdot 10^4$ liters/(mole cm).

When the yellowish green solutions of the dimers (If) and (Ig) are heated, they take on an emerald-green color; in the visible region, they show absorption by radicals formed by their thermal dissociation. The EAS of the radicals (IIf) and (IIg) are almost the same as the spectra of (IIa-d) (Fig. 1, Table 1). The values of ε and K can be found from Eq. (3) with adequate accuracy if there is a significant concentration of radicals; the greater the value of K, the smaller is the error in determining the intercept (value of ε) (Fig. 2). In this particular case, the concentration of 5-chloro-substituted radicals in MeCN at 340 K is adequate for a reliable calculation of ε (Fig. 2). The correctness of the determination of ε of the radical (IIf) is confirmed by the EPR data (Fig. 3).

The extinction coefficient ε of the radical (IIb) in MeCN (Fig. 2, Table 1) has the same value as in benzene. On the basis of this fact, in calculating the thermodynamic parameters of the equilibrium (1) in MeCN for the radicals (Ia-e), values were taken from [1], where they were found in benzene by means of EPR. An analysis of Table 1 indicates that the general form of the EAS of the radicals of type (II) is very little dependent on the solvent; and the extinction coefficient ε , as shown in the example of (IIb), is independent of the polarity of the solvent. However, the form of the EAS of the radical (IIe) differs from that of the others, owing to the auxochromic contribution of the substituent 5-NMe₂, which has an unshared electron pair on the N atom.

The long-wave band at 704-740 nm has positive thermochromism and solvatochromism. Upon heating from 293 to 353 K in the case of (IIa-d, f, g), a hypsochromic shift is observed, with a coefficient $\beta = d\lambda/dT = 0.06$ -0.08 nm/K, which is 2.5 times smaller than that in benzene ($\beta = 0.17$ nm/K). An analogous decrease in the thermochromic shift of the band in a polar solvent in comparison with a nonpolar solvent is also characteristic for cyanine dyes [11]. The solvatochromic effect is manifested to the greatest degree for the long-wave band of (IIa-d) (Table 2).

The thermodynamic parameters of the equilibrium, according to the EAS data (Fig. 3) are presented in Table 3. The Gibbs free energy ($\Delta G = -RT \ln K$) was determined from the values found for the equilibrium constant. The values of K, ΔH° , and ΔS° of the equilibrium (1) for (If) were also determined by EPR (Fig. 3, Table 3). Good agreement is observed between the results.

For all of the compounds (Ia-f), the Hammett equation gives a good description of the results (Fig. 4), with a coefficient of correlation r = 0.995. The equation $\Delta \log K = 1.53 \times \Sigma\sigma$ (where $\Sigma\sigma = \sigma_n + \sigma_m$) is a special case of the two-parameter equation $\Delta \log K = \rho_1 \sigma_n + \rho_2 \sigma_m$ with $\rho_1 = \rho_2 = \rho$. The positive value of ρ indicates an increase in thermodynamic stability of the radicals when they have electron-acceptor substituents. The influence of the substituent on captodative stabilization of radicals of the type of (II) has been examined in detail in [1, 6]. Since the value of ρ in MeCN (1.53) is considerably larger than in benzene (0.87), the constant K, when benzene is replaced by MeCN, increases to a greater degree for compounds with high values of σ . Thus, the value of K in MeCN in comparison with benzene for the halogen derivatives (Ib-d) increases by a factor of 30-40, but for (Ie), by a factor of only 5. The range of variation of K for the different dimers in MeCN is also considerably greater than in benzene (>10⁴ [1]). The higher value of ρ in MeCN is due to increased solvation of the radicals (II) in the polar solvent.

The rupture energy of the C^2-C^2 ' bond of the dimers (Ia-f) in MeCN is 51-75 kJ/mole in comparison with 77-85 kJ/mole in benzene. The higher value of K for (If) in comparison with (Ib-d) reflects mainly an increase in the entropy factor ΔS^0 ; whereas in the case of (Ig), which has a bulky substituent, the increase is due to a decrease in ΔH^0 .

The Hammett equation is also followed for the series (Ia-f), with individual constants $(\Delta \log K = 1.56 \Sigma \sigma^0)$, with a coefficient of correlation r = 0.987 (Fig. 4). Using electrostatically corrected values $\Sigma \sigma_{cor}^0$ for the NMe₃ group [12], we can evaluate the contribution of Coulomb interaction to dissociation of the dimer (If). It can be seen from Fig. 4 that $\Delta \log K$ does not correlate with $\Sigma \sigma_{cor}^0$, which reflects only the purely inductive effect after subtracting electrostatic interaction with the reaction center. This means that electrostatic interaction makes a larger contribution to the equilibrium constant K than does the inductive component; i.e., the electrostatic component is the decisive factor in increasing the thermodynamic stability of the radicals (II) as a result of Coulomb interaction in the system, which is related to the presence of the positively charged groups NR_3 .

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REACTION OF STANNOUS BIS-3,6-DI-TERT-BUTYL-0-SEMIQUINOLATE WITH PHENOXYL RADICALS

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An EPR study was carried out on the reaction of stannous bis-3,6-di-tert-butylo-semiquinolate with several phenoxyl radicals. An oxidative addition reaction may proceed with the formation of radicals with stannic ions. The reaction of biradical stannous complexes with 3,6-di-tert-butyl-2-hydroxyphenoxyl in the presence of triphenylphosphine in toluene gave a tin-containing free radical. The EPR spectra of this radical indicated rapid interligand exchange of the unpaired electron and bond.

Substituted o-quinones in organic solvents react with metallic tin to give stannous complexes with two paramagnetic o-semiquinolate ligands [1, 2].



The addition of an additional o-quinone molecule at tin in biradical (I) leads to biradical stannous complexes



This comprises the oxidative addition of o-quinone to stannous bis-o-semiquinolate.

In the present work, we showed that the oxidative additive may proceed as the result of the reaction of stannous bis-3,6-di-tert-butyl-o-semiquinolate with phenoxyl radicals



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