3. The enthalpy, entropy, and Gibbs energy of the reaction of phenyl glycidyl ether with diphenylcarbodiimide and phenylisocyanate were calculated. It was found that these processes are thermodynamically permissible over the whole temperature range studied and have an upper limiting temperature.

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THERMODYNAMIC PARAMETERS OF FREE RADICAL—DIMER EQUILIBRIA IN PHENYLINDANDIONE DERIVATIVES

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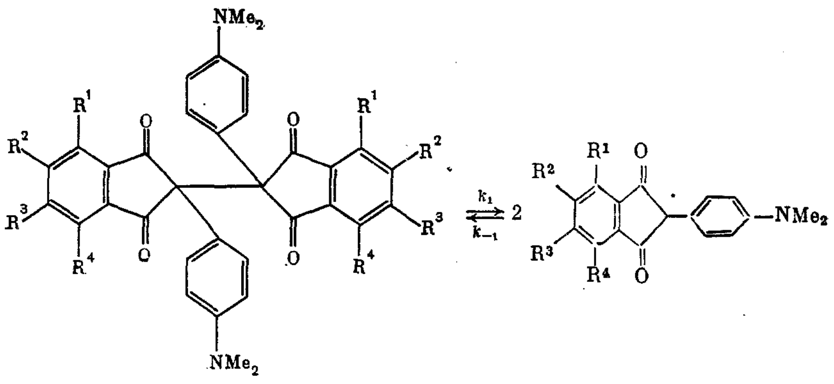
UDC 536.6:543.422.27:547.665

The present work relates to a study of equilibria between 2,2'-bis[R-2-(p-dimethylaminophenyl)indan-1,3-dionel (I) and the corresponding 2-arylindan-1,3-dione-2-yl radical (II)



(I) (II)

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TABLE 1. Thermodynamic Parameters for Free Radical–Dimer Equilibria*

Compound	From EPR spectra				From electronic spectra	
	ΔH°, kcal/mole	ΔS°, cal/mole·K	ΔG° (20°), kcal/mole	$K\cdot10^9$ (20%), mole/liter	ΔH°, kcal/mole	ΔS° †, cal/mole·K
(Ia)	19.3	22,8	12,6	0,40	19.2	22.4
(Ib)	18,8	23,2	12,0	1,08	18,8	23,2
(Ic)	18.3	22,4	11,7	1,90	18,4	22.8
(Id)	17,7	20,7	11,6	2.20	18,6	23,7
(Ie)	18,9	23,5	12,0	1.20	18,6	22.6
(If)	19,0	26,2	11,2	4.60	18.3	24,6
(Ig)	17,7	23,8	10,8	9,50	18.7	26.7
(Ih)	19,0	18,1	13,7	0,06	20.2	22.0
(Ii)	20,1	20,7	14,1	0,03	20,4	21.4

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*Accuracy of determinations: from EPR spectra, $\Delta H^0 \pm 0.5$ kcal/mole; $\Delta S^0 \pm 1.5$ cal/mole·K; from electronic spectra, $\Delta H^0 \pm 0.2$ kcal/mole; $\Delta S^0 \pm 0.6$ cal/mole·K.

†From the data for B (formula 2) where the extinction coefficient (ε) was obtained by using EPR data.

Interest in the dimers (I) arises from their strong inhibiting action on hydrocarbon oxidation [1] and from their thermo- and photochromic properties [2, 3]. For dimers with $R^1 = R^2 = R^3 = R^4 = H$ and $R^1 = R^2 = Cl$, $R^3 = R^4 = H$ it has been proved by proton and carbon-13 NMR spectroscopy that the structure is symmetrical about the $C^2-C^{2'}$ bond [4]. In inert organic solvents (II) occurs as kinetically unstable particles with a very high rate constant for recombination, $k_{-1} \sim 10^9$ liter/mole·sec [2, 3]. There is, however, definite thermodynamic stability in the system (I)-2(II) as a result of the high rate constant (k_1) for splitting of the dimer at the $C^2-C^{2'}$ bond.

We have studied the effect of substituents on the phthaloyl ring on the thermodynamic characteristics of the equilibrium of (I)-2(II) and also on the electronic absorption spectra of the dimers and the corresponding free radicals.

EXPERIMENTAL

The dimers (Ia-i) with different substituents on the phthaloyl ring were prepared by the methods of [5-7].

$R^1 = R^2 = R^3 = R^4 = H$(a), $R^1 = Cl$, $R^2 = R^3 = R^4 = H$(b), $R^2 = Cl$, $R^1 = R^3 = R^4 = H$(c), $R^2 = Br$, $R^1 = R^3 = R^4 = H$(d), $R^2 = I$, $R^1 = R^3 = R^4 = H$(e), $R^2 = CN$, $R^1 = R^3 = R^4 = H$(f), $R^1 = R^2 = R^3 = R^4 = Cl$(g), $R^2 = Me_2N$, $R^1 = R^3 = R^4 = H$(h), $R^1 = R^4 = Ph$, $R^2 = R^3 = H$(i).

The equilibrium (I) $\rightleftarrows$ (II) was studied by determining the concentration of (II) by ESR spectroscopy (in C_6H_6) and by the optical density in the electronic absorption spectra (in C_6H_6, $CHCl_3$, $MeCO_2Et$, DMSO, DMF).

The EPR spectra were recorded in evacuated ampuls on an RA-100 radiospectrometer using the X-band. The error in the determination of free radical concentration was ±10%. The temperature of the samples in the resonator was maintained to ±0.2°C by means of a liquid thermostat. The equilibrium constant was calculated from the formula

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

disregarding the value of $[(II)]/2 \ll [(I)]_0$.

The electronic spectra of the radicals were recorded on a Specord UV-VIS spectrophotometer, and in the case of very small equilibrium constants (Ii, h) on a Specord M-40 in quartz cells. The temperature of the cells was held to within ±0.1°C, the temperature being measured directly in the cell.

The electronic spectra of (IIa-i) were obtained by the method of [8]. According to formula (1), the following relationship holds for optical densities due to radicals (II)

$$\lg D^2/[(I)]_0 = -\Delta H^0/2.3RT + B \qquad (2)$$

where $B = \Delta S^0/2.3R + 2\log \varepsilon\ell$.

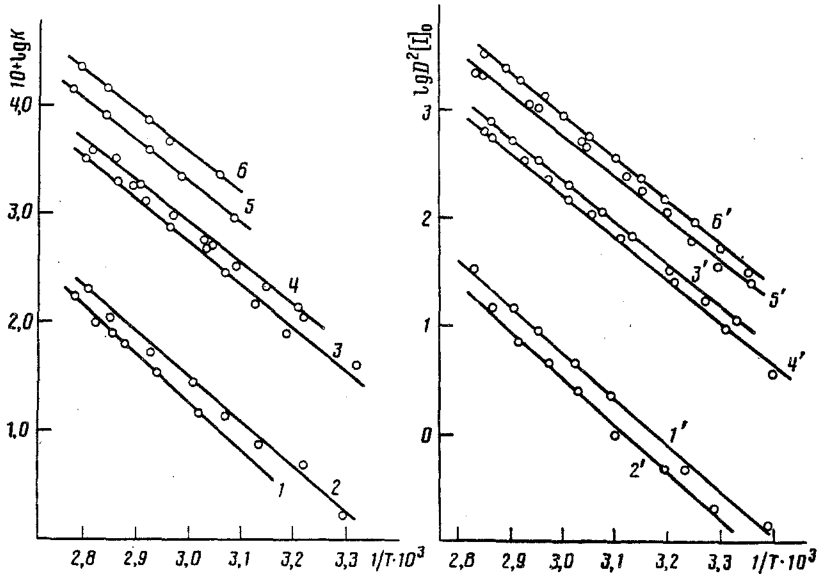

Fig. 1. Variation of equilibrium constants with temperature from EPR data (1-6) and values of $\log D^2/[(I)]_0$ in the long-wave absorption maximum of the radicals (1'-6') 1, 1') (Ii); 2, 2') (Ih); 3, 3') (Ie); 4, 4') (Id); 5, 5') (If); 6, 6') (Ig). Concentrations of dimers in EPR measurements (mole/liter): 1) $2.5 \cdot 10^{-2}$; 2) $1.01 \cdot 10^{-1}$; 3) $4.83 \cdot 10^{-2}$; 4) $1.04 \cdot 10^{-1}$; 5) $4.01 \cdot 10^{-4}$; 6) $4.13 \cdot 10^{-4}$. In electronic spectra: 1') $2.16 \cdot 10^{-4}$; 2') $3.8 \cdot 10^{-4}$; 3') $8.97 \cdot 10^{-4}$; 4') $7.07 \cdot 10^{-4}$; 5') $5.1 \cdot 10^{-5}$; 6') $4.13 \cdot 10^{-4}$. Solvent – benzene, $\ell = 3.1$ cm.

In the temperature range 20-90°C, all the changes in EPR and electronic spectra were reversible. The change in density of the solutions with temperature was taken into consideration in carrying out all the calculations [9]. The method of least squares was used to calculate ΔH^0 and ΔS^0 for the equilibria from the experimental results. The results obtained in the present work for (Id-i) are discussed together with the results [8] for (Ia-c).

RESULTS AND DISCUSSION

The thermodynamic equilibrium parameters derived from EPR (Fig. 1, lines 1-6) and electronic (Fig. 1, lines 1'-6') spectral data are shown in Table 1. The Gibbs free energy ($\Delta G^0 = -RT \ln K$) was determined from the values found for the equilibrium constant by EPR. For all the compounds (Ia-i) good agreement was found between values of ΔH^0 obtained by two independent methods. From the results obtained, the $C^2-C^{2'}$ bond splitting energy in the dimers varies only slightly with the type of substituent and amounts to $\Delta H^0 \cong 18\text{-}20$ kcal/mole.

Good agreement with the Hammett equation was obtained for all the compounds (Ia-i), with the correlation coefficient r = 0.992 (Fig. 2).

$$\Delta \lg K = 0.87 \Sigma \sigma$$

The large, positive value of the reactivity constant for this series (ρ 0.87) is evidence of a shift of electron density from the phenyl to the phthaloyl fragment in the radicals which significantly increases their stability (Table 1). The simultaneous presence in (II) of donor (Me_2N group on the phenyl ring) and acceptor (CO group and substituents on the phthaloyl ring) substituents at the radical center determines the captodative resonance stabilization of these radicals (cp [10]).

In the visible region of the electronic spectra of dimers (Ia-h) one intense maximum is observed at 340-380 nm (Table 2). The form of this band is independent of the type of substituent on the phthaloyl ring, only shift and a change in extinction coefficient ε occurring. The strong electron donor substituent Me_2N in (Ih) gives rise to an almost sevenfold increase in ε and has practically no effect on the position of the band [compare (lh) and (Ia)]. The strong electron acceptor substituents CN (If) and four atoms of Cl (Ig) on the other hand lead to a bathochromic shift of the band although ε does not change in comparison with the unsubstituted (Ia) (Table 2).

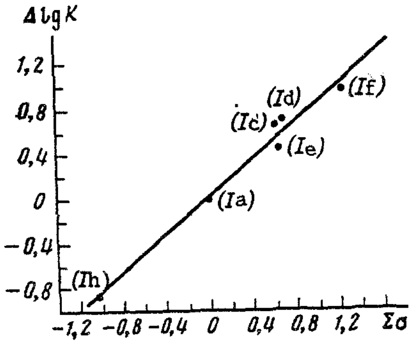

Fig. 2. Plot of log K against Hammett Σσ for the dimer–radical equilibrium in benzene at 20°C.

TABLE 2. Electronic Spectra of Dimers (Ia-i) in Benzene (20°C), λ, nm (log ε)

Dimer	λ_{max} (lg ε)	Dimer	λ_{max} (lg ε)	Dimer	λ_{max} (lg ε)
(Ia)	346 (3,96)	(Id)	360 (4,02)	(Ig)	380 (3,89)
(Ib)	360 (3,96)	(Ie)	360 (4,02)	(Ih)	340 (4,78)
(Ic)	360 (3,96)	(If)	377 (3,86)	(Ii)	Inflexion –

The electronic spectra of radicals (IIa-i) in the visible region are characterized by the presence of maxima in the 430-450, 625-660, and 700-770 nm regions (Fig. 3, Table 3). Independently of the type of substituent, a bathochromic shift of the bands is observed which is particularly strong (66 nm) for the long-wave band of (IIh) on account of the auxochrome effect of the n-electrons of the N atom of the substituent on the phthaloyl ring. For (IIh) a small hypsochromic displacement of a band to 625 nm and the appearance of a band at 578 nm are also observed, the latter showing as an inflexion in the spectra of the remaining radicals. The electronic spectrum of (IIi) which has bulky substituents in the positions ortho to the carbonyl groups does not differ from the spectra of (IIa-g).

The temperature dependence of the electronic spectra of the radicals was examined. For radicals (IIa-g, i), over the range from 20 to 80°C a hypsochromic displacement of 10 nm was observed only for the bands at 700-732 nm with coefficient $\alpha = d\lambda/d(T) = 0.17$ nm/degree. According to [11], temperature shift in electronic spectra results from changes in the physical character of the solvent. A small reduction of the dielectric constant (ε) occurs over the temperature range 30 to 80°C [12] which results in a reduction in the solvating ability of the benzene and hence to the appearance of a thermochromic shift. A similar effect – a strong temperature shift of bands in nonpolar solvents (toluene and methylcyclohexane) with small change in dielectric constant – has been observed for cyanine dyes [13]. A thermochromic shift was not experimentally detected for (IIh), probably because of the considerable reduction in charge transfer compared to the other radicals and also because of broadening of the bands. The dependence of the electronic spectrum of (IIa) on solvent type (Table 4) shows that both long-wave bands are subject to strong solvatochromism. The band at 700-770 nm has positive thermo- and solvatochromism and hence can be considered as a charge transfer band.

The equilibrium constant for the series of compounds examined varies by a factor of more than 300 at 20°C depending on substituent type (Table 1). The relationship between ΔH^0 and

TABLE 3. Electronic Spectra of Radicals (IIa-i) in Benzene (79.6°C), λ, nm (log ε)

Radical	λ_{max} (lg ε)
(IIa)	430 (4,22), 650 (4,04), 704 (4,15)
(IIb)	435 (4,32), 660 (4,12), 715 (4,23)
(IIc)	435 (4,26), 660 (4,07), 715 (4,20)
(IId)	440 (4,24), 660 (4,05), 720 (4,15)
(IIe)	440 (4,42), 660 (4,18), 720 (4,31)
(IIf)	450 (4,33), 660 (4,16), 732 (4,24)
(IIg)	450 (4,22), 666 (4,15), 729 (4,21)
(IIh)	434 (4,36), 578 (3,52), 770 (4,01) 625 (3,86)
(IIi)	444 (4,02), 640 (4,07), 700 (4,24)

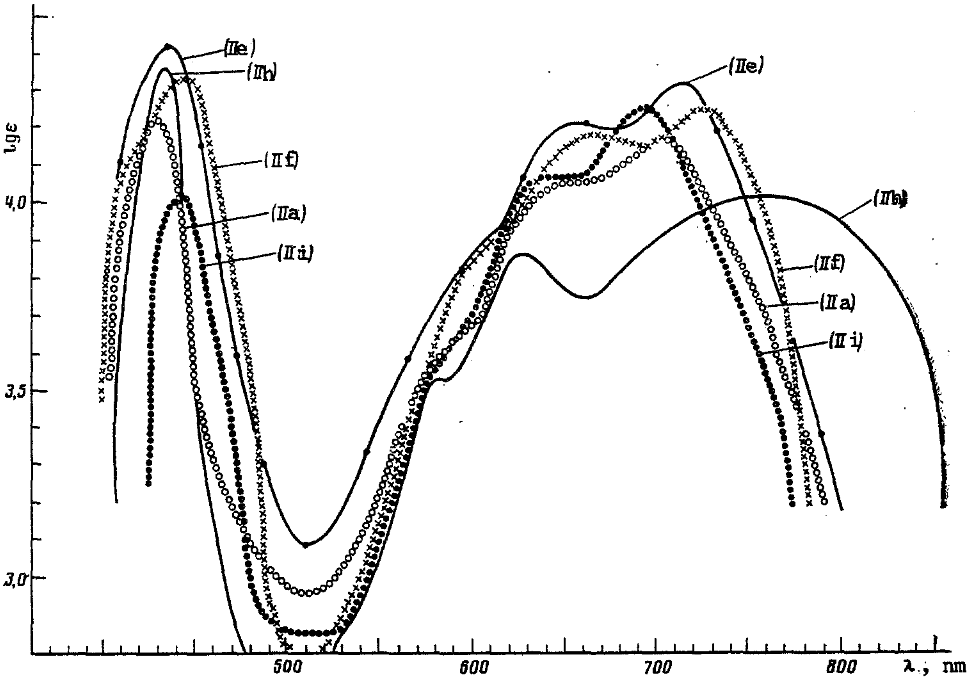

Fig. 3. Electronic spectra of radicals in benzene at 79.6°C.

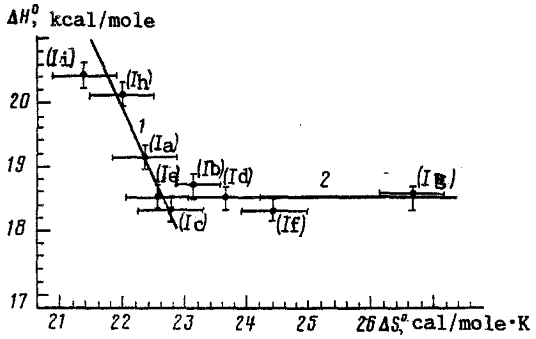

Fig. 4. Relationship of ΔH^0 and ΔS^0 for equilibria in the dimer–radical system in benzene with changes in the series of donor–acceptors (1) and and acceptors (2) from electronic spectrum data (Table 1).

TABLE 4. Dependence of the Electronic Spectra on the Dielectric Constant of the Solvent, 20°C

Solvent	Dielectric constant $(\varepsilon)^{(20°)}$	λ_{max}, nm
C_6H_6	2.28	647, 716
$CHCl_3$	4.80	652, 723
$MeCO_2Et$	6.02	652, 725
DMF	36.70	670, 741
DMSO	48.90	673, 746

ΔS^0 for dimers (Ia-i) is shown in Fig. 4 as a graph which can be considered as comprising two parts (1 and 2). On the graph the dimers are arranged strictly in order of monotonic change in equilibrium constant. On part 1 of the graph it is determined by differences in ΔH^0, on part 2 by changes in ΔS^0 since here ΔH^0 = constant. It is interesting that dimers with electron donor substituents are distributed along part 1, those with strong electron acceptor substituents on part 2, and dimers with weak electron acceptor substituents (halogens) at the meeting point of the two parts. Thus the introduction of electron acceptor substituents into the phthaloyl ring leads to a reduction in the stability of the dimers (increase in K) which is in agreement with the results of quantum-chemical calculations carried out for chlorine-substituted derivatives [14]. Electron donor and bulky substituents on the phthaloyl ring increase the stability of the dimers (reduction in K). The relationship between ΔH^0 and ΔS^0 for the equilibrium system (I)-2(II) studied is most unusual (Fig. 4). The most common relationship between these parameters is type of compensation effect. For example, for dimer–radical equilibrium in the case of triarylimidazolyl derivatives the analagous relationship between ΔH^0 and ΔS^0 is described, from the results of [15], by a straight line where these values change symbatically.

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CONCLUSIONS

Measurements of the thermodynamic parameters of the free radical—dimer equilibrium in benzene for 2,2'-bis[R-2-(p-dimethylaminophenyl)indan-1,3-diones] with different substituents R on the phthaloyl ring have been carried out. The equilibrium constants satisfy the Hammett equation ($\rho = 0.87$, benzene, 20°C). The bond breaking energy of the central $C^2-C^{2'}$ bond in the dimers amounts to ~18-20 kcal/mole The extinction coefficients of the 2-aryl-indan-1,3-dione-2-yl radicals in benzene have been determined. The long-wave band of the radicals displays thermo- and solvatochromism.

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KINETICS OF OXIDATION—REDUCTION DESTRUCTION OF TRISDIPYRIDYLRUTHENIUM (III) IN WEAKLY ALKALINE AND WEAKLY ACIDIC MEDIA

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Recently the problem of catalytic oxidation of water under the action of single-electron oxidants obtained with visible light has attracted much attention [1]. In this case the greatest attention has been devoted to the trisdipiridyl complex of ruthenium (III) Ru × $(Dipy)_3^{3+}$ [2]. It is well known, however, that accomplishment of the reaction

$$4Ru(Dipy)_3^{3+} + 2H_2O \xrightarrow{Cat} 4Ru(Dipy)_3^{2+} + O_2 + 4H^+ \quad (1)$$

encounters definite difficulties connected with the occurrence of side processes in which the oxidant is consumed in oxidation of organic compounds present in the system, in particular intrinsic ligands [3-5]; in the absence of catalysts all the $Ru(Dipy)_3^{3+}$ is consumed in oxidation of the ligands at any pH of the water solutions.

Oxidation—reduction destruction (ORD) of $Ru(Dipy)_3^{3+}$ has been studied previously [6, 7], but these investigations had a fragmentary character. An attempt at many-sided investigation of ORD of $Ru(Dipy)_3^{3+}$ was made in [8], where this reaction was studied in most detail in the pH 12-14 region. At the same time the pH region from 3 to 10 min which the maximum

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