HETERYLIMIDAZOLES

IV.* HOMOLYTIC DISSOCIATION OF HEXAARYLDIMIDAZOLYLS AND THEIR HETEROCYCLIC ANALOGS

Yu. A. Rozin, V. F. Gryazev,
V. E. Blokhin, Z. V. Pushkareva,
and G. É. Martina

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The rate constants and activation energies for homolytic dissociation of 2,2'-di[α(β)-naphthyl]-, 2,2'-diquinolinyl-, and 2,2'-di(9-acridinyl)-4,4',5,5'-tetraphenyldiimidazolyls in toluene in the presence of α,α-diphenyl-β-picrylhydrazine were determined. The degrees of dissociation of the diimidazolyls were found. The effect of substituents on the stability of imidazolyl radicals is discussed.

The effect of various substituents (substituted phenyl, naphthyl, and diphenylyl groups and residues of five-membered heterocycles) on the reactivities of imidazolyl radicals and on the ability of their dimers to undergo homolytic dissociation is well known [2].

We have studied the effect of residues of six-membered nitrogen-containing heterocycles on the dissociation of diimidazolyls in the case of 2,2'-diquinolinyl- and 2,2'-di(9-acridinyl)-4,4',5,5'-tetraphenyldiimidazolyls [3] (Table 1). 2-α and 2-β-Naphthyl-substituted diimidazolyls were investigated as model compounds.

The dissociation rate constants (k_{diss}) of diimidazolyls I-IX were measured by the method in [4], which is based on the reaction of the radicals formed in the reaction with α,α,-diphenyl-β-picrylhydrazine (X).

The process was followed spectrophotometrically from the increase in the optical density at λ = 530 nm – the absorption maximum of the radical of X (DPPH).

As in the case of aryl-substituted diimidazolyls [4], the kinetics of the formation of the DPPH radical are described by a first-order equation. The k_{diss} values obtained (Table 1) confirm the conclusion [2, 4] that the rate of dissociation of the diimidazolyl decreases as the electron-acceptor character of the substituent increases.

A study of the dependence of log k_{diss} on the σ constants of quinolinyl [6] and β-naphthyl substituents [7] showed that the σ constants found from the two reaction series (hydrolysis of the esters and the pK_a values of the corresponding quinolinecarboxylic acids) do not sufficiently accurately reflect the role of the factors affecting the stabilization of the transition state, which is apparently close to a radical state, in this process.

From the σ constants of two-ring substituents (Table 1), one should have expected a decrease in k_{diss} for all of the diimidazolyls containing such substituents as compared with 2-phenyl-substituted compound I. However, replacement of a phenyl group by an α-naphthyl group has little effect on k_{diss}, whereas

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*See [1] for communication III.

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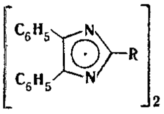
TABLE 1. Rate Constants for the Dissociation of Diimidazolyls (k_{diss}), Dissociation-Activation Energies (E_a), and Polarographic Oxidation Potentials of the Anions of the Corresponding Imidazoles ($E_{1/2}$)



Diimidazolyl	R	$k_{diss} \cdot 10^3$ min^{-1} ·					E_a, kcal/mole	σ, constants	$E_{1/2}$, mV
		50°	60°	70°	80°	90°			
I	Phenyl	—	6,8	19,0 (21,0)^2	56,8	148	24,7 (22,4)^2	0,0	465
II	1-Naphthyl	—	4,1	17,0 (21,6)^5	32,2	104	24,3 (15,8)^2	—	450
III	2-Napththyl l	18,9	85	129	414	—	23,2	0,17	435
IV	3-Quinolinyl	—	19,0	48	122	320	22,2	0,52	475
V	4-Quinolinyl	—	—	4,1	7,7	14,6	17,0	0,59	490
VI	5-Quinolinyl	—	7,0	23,9	64,6	128	22,5	0,37	460
VII	6-Quinolinyl	16,5	64	157	470	752	22,0	0,23	427
VIII	7-Quinolinyl	—	12,0	39	105	208	22,7	0,24	450
IX	9-Acridinyl	—	2,4	5,0	14,3	34,3	21,7	—	540

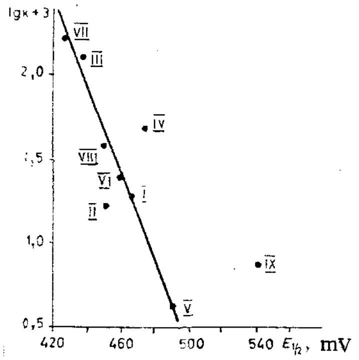


Fig. 1. Relationship between k_{diss} of diimidazolyls I-IX at 70°C in toluene and the potentials of polarographic oxidation of the anions of the corresponding imidazoles.

replacement by a β-naphthyl group leads to an increase in k_{diss} by a factor of 10-20. The aza analogs of the indicated substituents (quinolinyl groups) have a similar effect, whereas the effect of the nitrogen atom of the quinolinyl substituent on the remainder of the molecule is weakened. This is apparently due to the increased contribution of two-ring substituents to stabilization of the radical state as compared with the ionic state.

From a comparison of the k_{diss} values of 3-, 6-, and 7-quinolinyl-substituted diimidazolyls (IV, VII, and VIII) with the σ constants of the corresponding substituents, it can be concluded that the role of −M effects increases and the role of −I effects decreases. Replacement of the phenyl group in the 2 position of the imidazole ring of the diimidazolyls by a two-ring substituent is accompanied by a certain decrease in the activation energy (E_a) for their homolytic dissociation (Table 1).

A more strict relationship is observed between log k_{diss} and the half-wave potentials of polarographic oxidation of the anions of the corresponding imidazoles (Fig. 1). This constitutes evidence that the ability of the anion to undergo oxidation to an imidazolyl radical and the rate of homolytic dissociation of the diimidazolyls are determined to a considerable extent by the stability of the radicals formed. The point corresponding to acridinyl-substituted IX lies above the correlation line (Fig. 1). This can be explained by an increase in the steric hindrance in diimidazolyl IX, which promotes its dissociation into radicals. The decrease in its dissociation E_a value is in agreement with this.

In contrast to diimidazolyls I-IX, in the reaction of α,α-diphenyl-β-picrylhydrazine with 2,2'-di(6-quinolinyl)-4,4',5,5'-tetra(p-anisyl)diimidazolyl (XI) in toluene at 60° a discontinuity is detected on the semilogarithmic anamorphosis of the dependence of the optical density (D) on the time (τ) (Fig. 2). Inasmuch as there is a considerable concentration of the free radical at this temperature in the solution of XI, as indicated by the intense green color of the solution, it can be concluded that the first portion of the dependence of D on τ reflects primarily the kinetics of the reaction of the radical, which is in equilibrium with the dimer, whereas the second portion reflects the kinetics of dissociation of XI.

The rates of the first and second steps of the process were evaluated approximately. The k_{diss} values of XI were initially calculated from the second portion of the curve beginning with $\tau = 20$ min. The rate constant for the reaction of the imidazolyl radical with α,α-diphenyl-β-picrylhydrazine (k_{rad}) was then calculated as for a pseudomonomolecular reaction with allowance for this process. Under the given conditions, k_{rad} is 0.32 ± 0.02 min^{-1}, which is higher by a factor of 27 than k_{diss} for XI (0.0118 ± 0.0007 min^{-1}).

TABLE 2. Degree of Dissociation (α) of Diimidazolyls and Dimer–Radical Equilibrium Constants (K_{eq}) at 60°C and a Dimer Concentration in Toluene of 10^{-3} M

Diimidazolyl	Analytical wavelength, nm	ε	α	$K_{eq} \cdot 10^4$, mole/liter
I	551	517	0,20	2,15
II	745	113	0,22	2,61
III	707	160	0,78	70
IV	632	136	0,33	6,61
V	736	—	~0,01	~0,01
VI	690	100	0,19	1,70
VII	646	157	0,49	18,6
VIII	648	173	0,26	3,64
IX	551	152	0,16	1,22

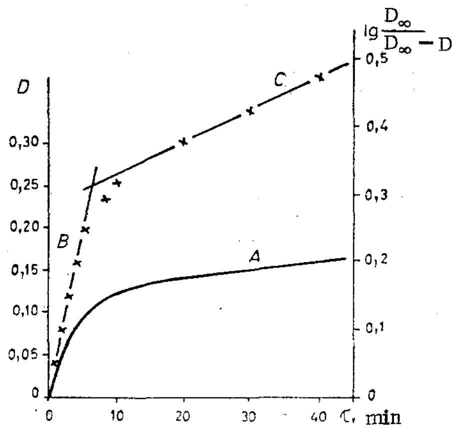


Fig. 2. Reaction of XI with diphenylpicrylhydrazine (DPPH). Dependence of the optical density on the time (A) and its anamorphosis (B and C) ($D_\sim$ = 0.24).

The radical–dimer equilibrium constants (k_{eq}) and the degree of dissociation (α) of the diimidazolyls were measured. The K_{eq} and α values in toluene at 60° for I-IX were determined by spectrophotometry from the optical densities of their solutions at λ_{max} of the long-wave absorption band of the radicals. Equilibrium was established in 15-20 min. The molecular extinctions (ε) were found from the dependence of the optical densities of the solutions under equilibrium conditions on the starting concentration of the dimer (Table 2). It is apparent from the data obtained that the effect of a substituent in the 2 position of the imidazole ring of the diimidazolyls on the radical–dimer equilibrium is similar to the effect on the rate of dissociation of the dimers – the degree of dissociation of the diimidazolyl decreases as the acceptor character of the substituent increases.

EXPERIMENTAL

The synthesis of the diimidazolyls was described in [3]. The oxidation potentials of the anions of I-IX were found [1] by polarographic oxidation of solutions of the corresponding imidazoles in dioxane containing a borate buffer (pH 9.18).

The optical densities of the solutions of diimidazolyls were measured in purified toluene with an SF-2M spectrophotometer in a thermostatted (with an accuracy of ±0.2°) cuvette with a thickness of 4 cm.

Solutions of diimidazolyls I-IX with an initial concentration of $3.8 \cdot 10^{-5}$ M were used to determine the rate constants of homolytic dissociation (k_{diss}). The α,α-diphenyl-β-picrylhydrazine concentration was $1.5 \cdot 10^{-4}$ M. The measurements were made at the absorption maximum of the DPPH radical (530 nm). The k_{diss} values were calculated from formula (1) with the aid of the method of least squares.

$$k_{diss} = \frac{2.303}{\tau} \lg \frac{D_\infty}{D_\infty - D}. \tag{1}$$

The accuracy in the determinations was 1-5%. The activation energies were found graphically with an accuracy of 10% from the dependence of log k_{diss} on T^{-1}.

The dimer–radical thermal equilibrium parameters were calculated from the formulas

$$C_R = \frac{D}{\varepsilon l}; \quad K_{eq} = \frac{C_R^2}{A - \frac{C_R}{2}}; \quad \alpha = \frac{C_R}{2A},$$

where C_R is the radical concentration under equilibrium conditions: A is the starting diimidazolyl concentration, D is the optical density of the solution, ε is the molecular extinction of the radical, and l is the thickness of the cuvette.

The ε values at the analytical wavelength were determined from the formula

$$\varepsilon = \frac{1}{2l} \cdot \left(\frac{D_1 - D_i}{\frac{A_i D_1}{D_i} - \frac{A_1 D_i}{D_1}} \right),$$

where D_1 is the optical density of the solution under equilibrium conditions for a starting diimidazolyl concentration (A_1) of 10^{-3} M, D_i is the optical density at concentration A_i (2, 4, 6, or $8 \cdot 10^{-4}$ M).

The accuracy in the determination of ε was 15%, and the accuracy in the determination of K_{eq} and α was 15-20%.

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