CHEMISTRY

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

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ACIDITY AND ENOLIZATION OF 2-ARYLINDANDIONES-1,3

Derivatives of indandione-1,3 are generally regarded as pseudoacids that form a diketone conjugate anion system in polar solvents and only the diketo form in aprotic solvents, since the existence of an enol form of these compounds had not been proved ([1]). The formation of enol ethers of indandiones-1,3 was explained by the theory of displacement of the reaction center ([2]).

We set ourselves the goal of investigating the acidity and the closely related problem of enolization ([3], [4]) of 2-arylindandiones-1,3.

The spectrophotometric method was chosen by us as the most reliable means of studying enolization ([5], [6]). Measurements were carried out on an SF-4 instrument in the range 215–500 mμ at $20 \pm 0.5°$. Keeping the solutions under study for 1 hour after preparation proved sufficient for attainment of equilibrium in all cases; usually equilibrium was established before this time (this was checked by repeated measurements of absorption intensity).

Fig. 1. U.-v. spectrum of 2-phenylindandione-1,3 and its enol ether: 1 –solution of 2-phenylindandione-1,3 in dichloroethane (diketone), 2 –solution of the methyl ether of 2-phenylindandione-1,3 in ethanol, 3 –solution of 2-phenylindandione-1,3 in ethanol containing 0.2 mole/l KOH (anion), 4 –solution of 2-phenylindandione-1,3 in 95% ethanol containing 0.1 mole/l HCl

Fig. 2. Relationship between the intensities of the diketone ε_D and enol ε_E maxima of 2-phenylindandione-1,3 in various solvents: 1 –dichloroethane; 2 –water (1% CH_3OH; 0.1 M HCl); 3 –50% ethanol (0.1 M HCl); 4 –95% methanol (0.1 M HCl); 5 –95% isobutanol (0.1 M HCl); 6 –95% ethanol (0.1 M HCl)

As a standard for the diketone form of 2-phenylindandione-1,3 (I), the spectrum of a solution of I in dichloroethane was recorded; the absorption spectrum of enol was represented by the spectrum of the methyl ether of I in alcoholic solution. The presence of a conjugate anion would have hindered detection of the enol; therefore acidified solutions were investigated. The presence of 0.1 M HCl in the solutions studied ensured practically complete suppression of the dissociation of I.

Solutions of I in benzene and dichloroethane showed practically no signs of enol; solutions of I in water and acetic acid had a somewhat increased absorption intensity in the visible region of the spectrum, which, apparently, should be attributed to the presence of the enol form. In solutions of acetone and dioxane, a noticeable decrease in the intensity of the diketone maximum of I was observed, together with the formation of an absorption band in the visible region of the spectrum. In alcoholic solutions of I, a considerable amount of di-

the ketone passed into another form (E), whose absorption differed from that of the enol ether (E) by a bathochromic shift (Fig. 1).

For a quantitative study of the composition of the tautomeric mixture I, we assumed that:

1) solutions of I in aqueous 0.1 M HCl contain not less than 98–99% of the diketone form (in the visible region $\varepsilon \sim 10$); 2) form E has, at the λ corresponding to the maximum of the diketone, $\varepsilon = 15000$ (similar ε values in this region are possessed by the enol ether and also by anion I); 3) the diketone form practically does not absorb in the visible region of the spectrum; 4) the concentrations of the diketone and E are in a simple linear dependence on one another (formation of a third form is excluded).

Table 1

Enolization of 2-phenylindandione-1,3 in various solvents

Solvent	Absorption: diketone maximum	Absorption: visible-region maximum	Enol content, %: by diketone max.	Enol content, %: by visible-region max.
Dichloroethane	228 (52800)	inflection 420–440 (0.5)		<0.05
Benzene		inflection 420–440 (1.6)		<0.2
Acetic acid		430 (30)		2
Dioxane		inflection 410–430 (80)		6

Solvent	Absorption: diketone maximum	Absorption: visible-region maximum	Enol content, %: by diketone max.	Enol content, %: by visible-region max.
Dioxane (5% H_2O)*	225.5 (43200)	428 (100)		8
Acetone		432 (140)		11
Acetone (5% H_2O)*	225 (42800)	435 (307)		24
Water	229 (50800)	inflection 420–460 (10)		<1
Ethanol/water (50% by volume)	228 (40700)	445 (310)	23	26
Methanol (5% H_2O)*	225.5 (41300)	440 (397)	29	31
Iso-butanol (5% H_2O)*	225.5 (33200)	440 (632)	48	49
Ethanol (5% H_2O)*	224.5 (30500)	440 (750)	58	58

* The solution contains 0.1 mol/l HCl.

The assumptions listed, together with the experimentally measured values of ε, made it possible to estimate the absorption intensity of pure E by a graphical method [7] (Fig. 2). The value $\lambda = 1300 \pm 100$ obtained for the long-wavelength maximum was used to estimate the amount of E in solutions I (Table 1). As further investigations showed, co-

Table 2

Acidity and enolization of $C_6H_4 < \substack{CO \\ CO} > CHC_6H_4R$

R	H_2O (1% CH_3OH): pK_{KE}	H_2O (1% CH_3OH): E, %	H_2O (1% CH_3OH): pK_K	50% C_2H_5OH: pK_{KE}	50% C_2H_5OH: E, %	50% C_2H_5OH: pK_T	50% C_2H_5OH: pK_K	50% C_2H_5OH: pK_E	95% C_2H_5OH: E, %	95% C_2H_5OH: pK_T
H	4.13	<1	4.13	4.42	25	0.48	4.29	3.82	58	–0.14
n-OCH_3	4.25		4.25	4.66	19	0.64	4.57	3.93	51	–0.02
n-$NHCOCH_3$	3.82		3.82	4.11	33	0.31	3.94	3.63	75	–0.48

Fig. 3. Correlation of the acidities of enols (b) and diketones (a) of 2-arylindandiones-1,3 with Hammett σ (50% ethanol)

Figure 3: Fig. 3. Correlation of the acidities of enols (b) and diketones (a) of 2-arylindandiones-1,3 with Hammett σ (50% ethanol)

R	H_2O (1% CH_3OH): pK_{KE}	H_2O (1% CH_3OH): E, %	H_2O (1% CH_3OH): pK_K	50% C_2H_5OH: pK_{KE}	50% C_2H_5OH: E, %	50% C_2H_5OH: pK_T	50% C_2H_5OH: pK_K	50% C_2H_5OH: pK_E	95% C_2H_5OH: E, %	95% C_2H_5OH: pK_T
n-SO_3^-	3.70	4	3.68	4.03	51	−0.02	3.72	3.74	81	−0.63
n-Cl	3.72		3.72	3.83	40	0.17	3.61	3.43	84	−0.72
n-$N^+(CH_3)_3$	2.66	5	2.64	2.84	60	−0.18	2.44	2.62	93	−1.12
n-NO_2	2.39	16	2.31	2.20	72	−0.41	1.63	2.04	95	−1.28
m-OCH_3	3.98		3.98	4.18	23.5	0.51	4.06	3.55	51	−0.02
m-Cl	3.51		3.50	3.72	42	0.14	3.48	3.34	79	−0.58
o-OCH_3	5.61		5.61	6.61	0.7	2.15	6.61	4.54	1.6	1.77
o-Cl	4.11		4.11	5.11	4.7	1.31	5.09	3.78	12	0.86

the amount of E does not depend on the concentration of acid in the solution, if the ionic strength $\mu < 0.5$ and formation of the anion does not occur. Upon addition of acid or of a neutral electrolyte (KCl) in high concentrations (1 M and higher), a decrease in the concentration of E was observed. Changing the concentration of I within the range from 10^{-4} M to $5 \cdot 10^{-3}$ M did not affect the relative amount of E in the solutions.

For the study of the tautomeric equilibria of other 2-arylindandiones-1,3 we used water (containing 1% CH_3OH), 50% (by volume) aqueous ethanol, and 95% ethanol—solvents with different enolizing ability (Tables 1, 2). The content of E in aqueous solutions of 2-arylindandiones-1,3 was estimated only in individual cases because of the low degree of enolization and the very limited solubility of most 2-arylindandiones-1,3 in water; enolization in the other two solvents was studied similarly to the enolization of I (see above).

Fig. 3. Correlation of the acidities of enols (b) and diketones (a) of 2-arylindandiones-1,3 with Hammett σ (50% ethanol)

The acidity of 2-arylindandiones-1,3 in aqueous solutions was determined according to a previously developed method (8). In determining the protolysis constants of the keto-enols (K_{KE}) in 50% ethanol, the pH of partially neutralized solutions was measured using glass (Radiometer G 200C) and calomel electrodes calibrated against aqueous standards; for the study of less stable substances a spectrophotometric method was used (8). The values of pK_{KE} were calculated with corrections for hydrolysis and for the salt effect. Measuring, for control purposes, the acidity of benzoic acid in 50% ethanol, we obtained $pK = 5.67 \pm 0.03$, which is in satisfactory agreement with the data of other authors (9). All investigations were carried out in a thermostated room at $20 \pm 0.5^{\circ}$. The reproducibility of the pK_{KE} measurements lay within ± 0.03 for aqueous and ± 0.05 for aqueous-alcoholic solutions; the relative error in determining the amount of enol did not exceed $\pm 10\%$, which corresponds to ± 0.04 pK_{T} units at small and ± 0.08 at average (50%) amounts of enol. The acidities of the enolic (K_{E}) and diketonic (K_{k}) forms in 50% ethanol were calculated according to (3,4) (Table 2).

As is seen from the data of Tables 1 and 2, solutions of 2-arylindandiones-1,3 in dioxane, acetone, and especially in alcohols reveal the presence of a considerable amount of the tautomeric form E, which, in our view, has the structure of an enol polarized as a result of the formation of intermolecular hydrogen bonds with the solvent (P). The formation of such bonds changes the distribution of electron density in the enol system toward A, thereby decreasing the strain of the five-membered enol ring and promoting the enolization of 2-arylindandiones-1,3 in proton-acceptor solvents.

$$\mathrm{O{=}C{-}C{=}C{-}O{-}CH_3} \qquad \underset{\mathrm{E}}{\mathrm{O{=}C{-}C{=}C{-}O{-}H\cdots P}} \qquad \underset{\mathrm{A}}{\mathrm{O{=}C\cdots C{=}O}}$$

Unexplained, however, is the very low enol content in aqueous solutions of 2-arylindandiones-1,3. Russell[10] explains a similar phenomenon in the enolization of β-cyanoketones by the solvation effect of the ketone form. It is possible that hydration of the diketo form also decreases enolization in the case of 2-arylindandiones-1,3.

Figure 3 shows the correlation, calculated by us, of the acidities of the tautomeric forms of substituted 2-arylindandiones-1,3 with the Hammett σ constants (for R $= p\text{-NO}_2$ we used $\sigma = +1.270$)[11]. Despite deviations from linearity, it is clearly seen that substituents in the phenyl radical affect C-acidity more strongly than O-acidity; this agrees with the fact that the introduction of electron-acceptor substituents into phenyl radical I increases enolization.

The decrease in acidity of I upon *o*-substitution we explain by disruption of the coplanarity of the molecule.

To determine the range of applicability of the regularities derived by Kabachnik and Ioffe[12] in the case of 2-arylindandiones-1,3, graphs were constructed (Fig.

Fig. 4. pK of protolysis of the diketone forms of 2-arylindandiones-1,3 in water (pK_{K1}) and 50% ethanol (pK_{K2}) (solid line); pK of tautomeric equilibria of 2-arylindandiones-1,3 in 50% (pK_{T2}) and 95% ethanol (pK_{T3}) (dashed line).

Figure 4: Fig. 4. pK of protolysis of the diketone forms of 2-arylindandiones-1,3 in water (pK_{K1}) and 50% ethanol (pK_{K2}) (solid line); pK of tautomeric equilibria of 2-arylindandiones-1,3 in 50% (pK_{T2}) and 95% ethanol (pK_{T3}) (dashed line).

4). It is seen that the acidity and enolization of the compounds studied by us in different solvents show a linear dependence, but the angles of inclination are not equal to 45°, as has also been noted in other cases[13]. The results obtained show that 2-arylindandiones-1,3 constitute a class of such trans-fixed β-diketones in which, according to Eistert' s concepts, the enol content depends on the type of solvent[14,15].

Fig. 4. pK of protolysis of the diketone forms of 2-arylindandiones-1,3 in water (pK_{K1}) and 50% ethanol (pK_{K2}) (solid line); pK of tautomeric equilibria of 2-arylindandiones-1,3 in 50% (pK_{T2}) and 95% ethanol (pK_{T3}) (dashed line).

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Note: Figure translations are in progress. See original paper for figures.