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Dissociation Constants of the Cyanohydrins of Substituted Acetonaphthones

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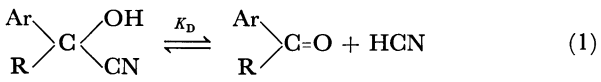
Synopsis. The dissociation constants of the cyanohydrins of 4-substituted 1-acetonaphthones and 6-substituted 2-acetonaphthones were determined at 30 °C in 80% dioxan-water(v/v). 1-Acetonaphthone Cyanohydrin has a greater dissociation constant than 2-acetonaphthone cyanohydrin due to steric interaction between the reaction centre and *peri*-H. The Hammett equation is well obeyed by both the series. The ρ values are found to be -1.18 and -2.36 for the 1-series and the 2-series respectively. The significant difference in the ρ values suggests that the electronic transmission is different in these two cases.

The position of equilibrium in the reversible dissociation of cyanohydrins of aralkyl ketones (Eq. 1) is governed by both steric and electronic effects. Steric



(1)

strain in the cyanohydrin favours the dissociation since there is a change in the coordination of the reaction centre from tetrahedral to trigonal.[1] The carbonyl group can mesomerically conjugate with the aryl group and stabilise the product. Hence electron-donating substituents in the aromatic ring favour the dissociation while the reverse is the case for electron-attracting substituents.[2] This is borne out by the negative ρ value obtained for the dissociation of the cyanohydrins of *meta*- and *para*-substituted benzaldehydes.[3] In an attempt to understand the degree of electronic transmission in substituted acetonaphthones, we measured the dissociation constants of the cyanohydrins of 4-substituted 1-acetonaphthones and 6-substituted 2-acetonaphthones. We report herein our results.

Experimental

Material. The substituted acetonaphthones were prepared by known methods.[4] Commercial dioxan was refluxed with 1M hydrochloric acid (100 ml for 1 litre of dioxan) with occasional passing of air, treated with excess sodium hydroxide and distilled. It was finally fractionated over sodium.[5] Doubly distilled water was used for all purposes. Solutions of HCN were obtained by mixing equal volumes of equimolar solutions of potassium cyanide and perchloric acid in the reaction medium and decanting the clear solution from precipitated potassium perchlorate.

Determination of Equilibrium Constants. The titrimetric method of Lapworth and Manske[6] was followed. The required quantity of the ketone was weighed into a volumetric flask (50 ml), dissolved in a small amount of the solvent and treated with exactly 20.0 ml of the stock solution of HCN. A 2% solution of piperidine (1 ml) was then added and the volume was made up to 50 ml. The flask was stoppered, sealed with paraffin wax and kept in a thermostat at 30 °C for 36 h. At the end of this period, the unreacted hydrogen cyanide was estimated by pipetting out aliquots (10 ml) into a known excess of silver nitrate containing 1% HNO_3 and back titrating with ammonium thiocyanate. A blank run was carried without the ketone in order to determine the initial concentration of HCN. The dissociation constant K_D, was calculated from the relation,

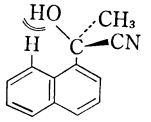
$$K_D = \frac{(a-x)(b-x)}{x},$$

where a is the initial concentration of ketone, b is that of HCN and x is the equilibrium concentration of cyanohydrin.

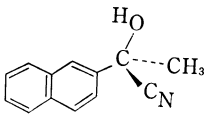
Results and Discussion

In Tables 1 and 2 are given the dissociation constants of the cyanohydrins of 4-substituted 1-acetonaphthones and 6-substituted 2-acetonaphthones respectively.

The data indicate that the cyanohydrin of 1-acetonaphthone (I) dissociates to a greater extent than that of 2-acetonaphthone (II). In the case of I, interaction



I



II

with adjacent *peri*-H is relieved on dissociation leading to a higher K_D value; such an interaction is absent in II. Based on the electronic effect of the 2,3-benzo group($\sigma=0.5$) and 3,4-benzo group($\sigma=0.04$)[7] alone, one would expect the cyanohydrin of 2-acetonaphthone to dissociate to a greater extent. Our present results obviously indicate that steric effect outweighs the electronic effect in this reaction.

The Hammett equation is obeyed both by 1- and 2-series (Figs. 1 and 2). The ρ value is found to be -1.18($r=0.997$) for the dissociation of the cyanohydrins of 4-substituted 1-acetonaphthones and -2.36 ($r=0.991$) for the dissociation of 6-substituted 2-acetonaphthone cyanohydrins. For the Hammett plots, the

TABLE 1. DISSOCIATION CONSTANTS OF THE CYANOHYDRINS OF 4-SUBSTITUTED 1-ACETONAPHTHONES IN 80% DIOXAN-WATER(V/V) AT 30 °C

Substituent	$K_D \times 10^2$ mol/l
H	19.1
F	16.0
Cl	11.4
Br	10.8
CH_3	28.5
OCH_3	52.2

Table 2. Dissociation constants of the cyanohydrins of 6-substituted 2-acetonaphthones in 80% dioxan-water (v/v) at 30 °C

Substituent	$K_D \times 10^2$ mol/l
H	9.59
F	7.55
Cl	6.00
Br	5.35
SCH_3	8.44
SO_2CH_3	1.55
CH_3	21.9
OCH_3	31.5

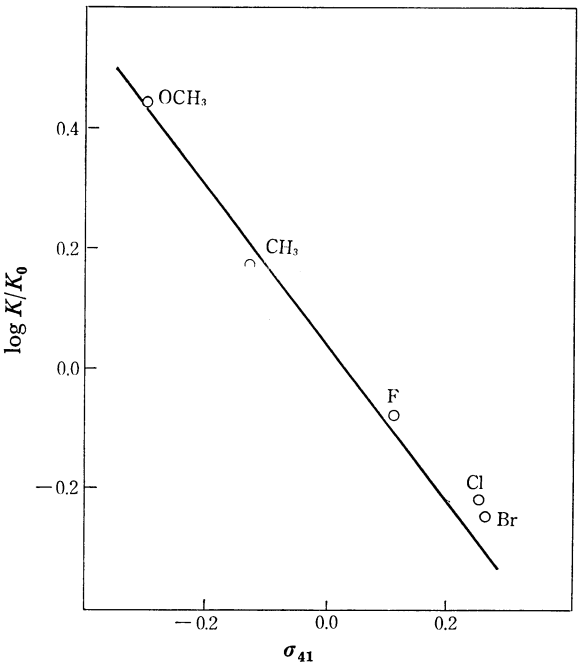


Fig. 1. Hammett plot of 4-substituted 1-acetonaphthones.

σ constants derived by Baliah and Ananthakrishna Nadar[4] were used. In 1-acetonaphthone the acetyl group has a difinite tendency[8] to go out the plane of the aromatic ring due to the *peri*-H. Owing to the difficulty in attaining coplanarity the mesomeric interaction of the acetyl group with the ring will be less in 1-acetonaphthones than in 2-acetonaphthones. This is reflected in a smaller ρ value for the 1-series than that for 2-series. A similar result was obtained by

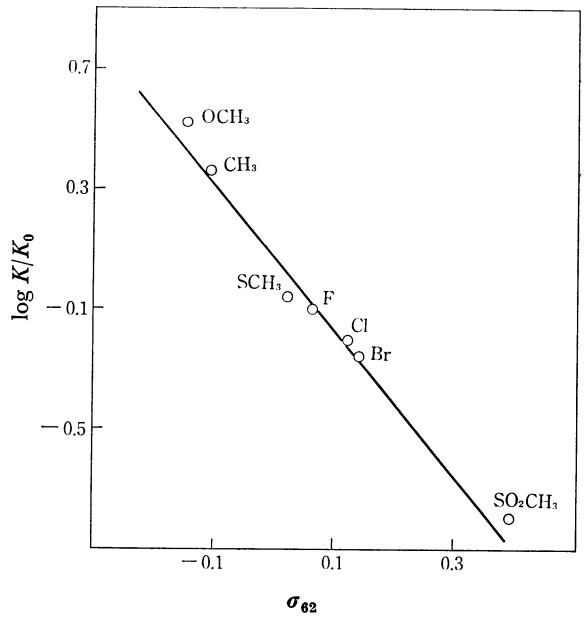


Fig. 2. Hammett plot of 6-substituted 2-acetonaphthones.

us in the reduction of substituted acetonaphthones by sodium tetrahydroborate[9].

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