The Acidities of Weak Acids. Part IV.[1] Some Methyl Styryl Ketones

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A series of ring-substituted methyl styryl ketones ($XC_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3$) have been synthesised and their acidities measured at 298.2 K using solutions of tetramethylammonium hydroxide (0.011 M) in dimethyl sulphoxide–water mixtures. In most cases the rates of detritiation in aqueous hydroxide ion solutions have also been measured. The results show that these compounds obey the same pK_a–$\lg k^T_{OH^-}$ relationship as was established for the structurally similar acetophenones.

The development of highly basic media has made possible the determination of fairly weak acidities ($12 < pK_a < 30$) and since the rates of ionisation of carbon acids are greatly accelerated in these solutions the linear free-energy relationship established by Pearson and Dillon[2] for the relatively strong carbon acids can be extended to these compounds. Inherent in this task is the problem of how severe a structural modification can be made to an acid before it begins to depart from such a relationship. In addition the difficulty of obtaining structurally similar compounds that cover a wide reactivity range is well known.

Relatively few studies of rate–equilibria correlations in highly basic media have been reported. For fluorene-type hydrocarbons,[3] tritium exchange rates in methanolic sodium methoxide are linearly related to the pK_a values in the caesium cyclohexylamide–cyclohexylamine system with a Brönsted exponent of 0.37, whereas similar studies for polyarylmethanes[4] give a value of 0.58. Cram and Kollmeyer[5] reported a curved Brönsted plot for the same kind of acids in a 75% MeOD–25% $(CD_3)_2SO$ medium but this interpretation rests heavily on the results for fluorene. The pK_a values of several fluorinated benzenes have been measured and as the tritium exchange rates of the *ortho*-, *meta*-, and *para*-hydrogens in fluorobenzene with lithium cyclohexylamide–cyclohexylamine relative to benzene have been shown to be almost identical with the partial rate factors for exchange of *ortho*-, *meta*-, and *para*-fluorine substituents in tritium exchange from polyfluorobenzenes in methanolic sodium methoxide solutions, this has made possible an estimate of 43 for the pK_a of benzene[6] itself. Similarly a pK_a value of 40.9 for toluene can be estimated from the rates of tritium exchange of several aryl- and polyarylmethanes when correlated with the known pK_a values.[7]

In some of these studies ion-association effects are important and the rate and equilibrium measurements do not refer to the same solvent. In our previous work on the acetophenones[8] the first effect is absent and the second minimised by using purely aqueous conditions for the rate measurements and dimethyl sulphoxide–water mixtures for the acidity determinations. In extending the work to compounds having the same structural features as the acetophenones but which cover a much wider reactivity range we have synthesised compounds of the type $XC_6H_4{\cdot}CH{:}C(Y){\cdot}CO{\cdot}CH_3$—the present paper is however concerned with the case Y = H, compounds whose acidities and rates of ionisation are expected to be very similar to the acetophenones.

EXPERIMENTAL

Materials.—The methyl styryl ketones were all prepared by the same method, namely condensation between the appropriate benzaldehyde and acetone in the presence of sodium hydroxide, although the experimental conditions varied slightly from compound to compound in accordance with previously published work. Thus the *meta*-methoxy-compound was prepared as in Heilbron and Hill's[9] paper whereas the *meta*-bromo- and *meta*-chloro-compounds were prepared using the conditions specified by Bauer and Vogel;[10] for the other compounds the experimental conditions were as described by Lutz and his co-workers.[11] The purity of the compounds was ascertained by microanalysis and either by m.p. or b.p. determination.

Reagent grade dimethyl sulphoxide was purified by distillation under reduced pressure in the presence of nitrogen and stored over 4A molecular sieves. G.l.c. analysis showed <0.1 wt % water.

Stock tetramethylammonium hydroxide solutions were made up at frequent intervals by addition of the solid pentahydrate to freshly distilled deionised water. The highly basic media comprising dimethyl sulphoxide, water, and tetramethylammonium hydroxide were made up by weight, the hydroxide ion concentration being 0.0110M. A stock carbonate-free sodium hydroxide solution was used for the kinetics.

9-t-Butylfluorene was the 'standard' acid used in the determination of the ketone acidities. Its preparation has been described[12] as has that of the tritium-labelled form.[13] The tritiated methyl styryl ketones were also prepared by the same procedure. In one instance it was confirmed by

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tritium n.m.r. spectroscopy that the label was entirely in the methyl group.[14]

Acidity Determination.—The method used to determine the acidities of the methyl styryl ketones is the same as that employed previously and has been described in detail.[15] The uncertainty in any of the pK_a values (±0.1—0.2) is the same as was found for the acetophenones.

Kinetics.—The procedure for following the rates of detritiation has been given.[16] In general reactions were studied to more than 80% completion and it was customary practice to vary the hydroxide ion concentration by a factor of 3—5. The second-order rate constants ($k^{\mathrm{T}}_{\mathrm{OH^-}}$) were reproducible to within ±1—3%.

Acidities and detritiation rate constants for some methyl styryl ketones at 298.2 K

	Substituent	pK_a in Me_2SO-H_2O mixtures	$10^4k^{\mathrm{T}}_{\mathrm{OH^-}}$ / $dm^3\ mol^{-1}\ s^{-1}$ (in H_2O)
(1)	*p*-OMe	22.09 ± 0.1	25.1
(2)	*m*-OMe		35.0
(3)	H	21.65[a] + 0.1	33.7
(4)	*p*-Br	21.60 ± 0.2	46.1
(5)	*p*-Cl	21.42 ± 0.1	45.1
(6)	*m*-Cl	21.37 ± 0.1_5	48.1
(7)	*m*-Br	21.23 ± 0.1	48.4
(8)	*p*-CN	20.65 ± 0.1	85.7
(9)	*m*-NO_2		72.4
(10)	*p*-NO_2		101

[a] 0.25 pK Units less acidic than previously reported.[17]

RESULTS AND DISCUSSION

As expected the interposing of the vinylic linkage between the benzene ring and the acetyl group reduces the effect which a substituent in the ring has on both the acidities and the rates of ionisation of the methyl styryl ketones. The pK_a values, which cover no more than 1.5 units, are linearly related to the Hammett substituent constant σ with a slope (ρ) of 1.42 ± 0.1. The value is approximately three times lower than that found for the acetophenones.[8] Similarly the plot of lg $k^{\mathrm{T}}_{\mathrm{OH^-}}$ against σ is also linear with a slope of 0.55 ± 0.03, approximately half the value for the acetophenones. Results similar to these have been reported for other systems. Thus in the case of cinnamic acids [18] ($ArCH{:}CH{\cdot}CO_2H$) the slope of the pK_a–σ plot is 0.42, similar to that reported for 1-aryl-2-nitropropanes ($ArCH_2{\cdot}CHMe{\cdot}NO_2$) in 50% (v/v) water–methanol (0.395) which itself is considerably lower than that reported for 1-arylnitroethanes ($ArCHMe{\cdot}NO_2$) (1.07) under the same conditions.[19] In the rates of ionisation of the 1-aryl-2-nitropropanes the value of ρ is 0.66_5, and for the 1-arylnitroethanes, 1.44.[19]

The factor of *ca.* 3 for the difference in the ρ values for acetophenone and methyl styryl ketone ionisation, and a corresponding value of *ca.* 2, for the kinetic process does not indicate a differential effect as the pK_a–σ plot for the acetophenones, which covered a much wider range of pK_a values, was distinctly curved. This being so the results for the methyl styryl ketones fit the same Brönsted relationship as was established for the acetophenones, the slope over the pK_a region 20.6—22.1 being 0.36 ± 0.03. These results do, therefore, tend to confirm those previously obtained for the acetophenones and establish more firmly the form of the Brönsted relationship in the above pK_a region.

Support from the S.R.C. (to T.G.R.) is gratefully acknowledged.

[5/2029 *Received*, 17*th October*, 1975]

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