Tetrahedron Letters No. 20, pp. 1663-1664, 1971. Pergamon Press. Printed in Great Britain.

pK_{AH}-VALUES OF NITRILES, tert.-BUTYL ESTERS AND DIMETHYLAMIDES OF SOME PHENYLACETIC ACIDS

K. Zaharieva, J. N. Stefanovsky and I. G. Pojarlieff
Institute of Organic Chemistry, Bulgarian Academy of Sciences,
Sofia 13, Bulgaria

(Received in UK 23 March 1971; accepted in UK for publication 6 April 1971)

Data on the acidities of phenylacetic acid derivatives have been reported only for some nitriles. Much attention has been devoted to 4-nitrobenzyl cyanide, pK = 13.45, as an indicator spanning the pH with the H_--regions. It has been shown,[1] however, that the spectra of this compound undergo complicated changes depending on the kind of solvent and on the amount of base and is therefore unsuitable as an indicator. Other arylsubstituted acetonitriles, amongst which 3-chlorobenzyl cyanide, pK = 18.10 in aqueous DMSO, were found to ionize normally. There is NMR-evidence that 4-nitrobenzyl cyanide also undergoes ionization by proton loss in ethanolic DMSO and in ethylenediamine/DMSO.[2] The pK's of some benzyl cyanides with electron withdrawing substituents have been determined in aqueous NaOH:[3] 4-cyano - 14.47: 4-nitro-3,5-dimethyl - 13.44; 4-nitro - 13.35. These data afforded a Hammett ρ-value of ca. 4 and an extrapolated value for the pK of benzyl cyanide of 18.

The pK-values listed on Table 1 were determined in aqueous DMSO containing 0.011M tetramethylammonium hydroxide using the H_--function of Dolman and Stewart.[4] The ionization ratio was determined by measuring the absorbance of solutions of various H_--values at λ_{max} of the anions using essentially

Table 1. pK_{AH}-values of phenylacetic acid derivatives

Nitriles		tert.-Butyl esters		Dimethylamides	
4-Chloro	19.39	4-Bromo	20.79	4-Bromo	23.43
Unsubstituted	20.78	4-Chloro	21.18	4-Chloro	23.63
4-Methyl	21.20	Unsubstituted	22.40	Unsubstituted	24.73
4-Methoxy	22.16	4-Methyl	22.73		
		4-Methoxy	23.49		

the technique of Stewart and O'Donnell[5] for work under oxygen-free conditions. The absorbance of the solutions in which ionization occurred decreased with time, the rate of decrease being greatly enhanced in the presence of traces of oxygen. The ionization ratios were obtained from the absorbance values extrapolated to the time of mixing. Only in the case of the nitriles at H_--values lower than the pK, the absorbance increased with time reaching a plateau, remained constant for a longer time than that needed to attain the plateau and then began to decrease. In this case the absorbances at the plateaus were taken into account. Plots of $\log\frac{[A^-]}{[AH]}$ vs. H_- were linear with slopes close to unity varying from 0.80 to 1.25, the deviations being probably due to experimental error rather than non-observance of the H_--function (see also [6]).

The pK-values obtained correlate satisfactorily with Hammett's σ^--values. The following ρ-values were obtained including the data for 3-chlorobenzyl cyanide from [1]: nitriles, $\rho = 5.85$ ($r = 0.985$); tert.-butyl esters, $\rho = 4.82$ ($r = 0.980$); dimethylamides ρ ca. 5.15.

References

1. R. Stewart, J. P. O'Donnell, K. Bowden, Can. J. Chem., 43, 1225 (1965)
2. M. R. Crampton, J. Chem. Soc., B, 85 (1967)
3. E. Feytmans-de Medicis, A.Bruylants, Bull. Soc. Chim. Belg., 75, 691 (1966)
4. D. Dolman, R. Stewart, Can. J. Chem., 45, 911 (1967)
5. R. Stewart, J. P. O'Donnell, ibid., 42, 1681 (1964)
6. K. Bowden, R. Stewart, Tetrahedron, 21, 261 (1965)