Protonation Equilibria of Ureas

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Summary The basicity constants pK_{BH^+} of phenylurea and five substituted phenylureas have been measured and their protonation equilibria have been found to follow the H_A acidity function.

It is now widely accepted that the H_0 acidity function does not uniquely describe the protonation behaviour of indicators of different structures and especially those with different basic sites. Many new acidity scales have been formulated, one of which, H_A, has been found to explain the protonation equilibria of amides,[1] pyridine 1-oxides,[2] sulphoxides,[3] carbamic acid esters,[4] and αβ-unsaturated aldehydes, ketones, and carboxylic acids.[5]

At present there are few quantitative data on the basicity constants of ureas. Hall[6] predicted a value pK_{BH^+} of -0.03 for phenylurea from measurements in glacial acetic acid, but Perrin[7] in his review on basicity constants classifies this value as unreliable. Moodie and Farlow[8] have recently estimated values of pK_{BH^+}, based on the H_0 scale, for urea and ethylurea as -0.15 and 0.00 respectively.

We now report values of pK_{BH^+} for six phenylureas, and find that their protonation equilibria follow the H_A acidity function. The Table gives the values of pK_{BH^+} for phenylurea, and for five substituted phenylureas, the slopes [$d\log_{10}I/d(-H_A)$] and correlation coefficients (c.c.) of plots of $\log_{10}I$ *vs.* $-H_A$, the slopes [$d\log_{10}I/d(-H_0)$] of plots of $\log_{10}I$ *vs.* $-H_0$, and the percentage (w/w) of H_2SO_4 at half protonation. The ionisation ratio $I = [BH^+]/[B]$ was measured spectrophotometrically using a combination of the methods of Davis and Geissman[9] and of Katritzky *et al.*[10]

Ionisation data for phenylureas ($R{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$) *in sulphuric acid at* 25·0 °C

R	$-pK_{BH^+}$	$d\log_{10}I/d(-H_A)$	C.c.	$d\log_{10}I/d(-H_0)$	% w/w H_2SO_4 at $[BH^+] = [B]$
H	1·30	0·95	0·998	0·69	26·2
4-F	1·18	1·04	0·994	0·89	24·0
4-Cl	1·48	0·95	0·997	0·68	29·8
4-Br	1·57	1·05	0·995	0·66	31·7
4-Me	1·22	0·98	0·996	0·85	24·8
3-Me	1·18	0·99	0·996	0·77	24·0

It is a necessary, but not sufficient, criterion that for values of pK_{BH^+} to be thermodynamic basicity constants, plots of $\log_{10}I$ *vs.* acidity function $-H$ should have unit slope. Yates and Stevens[11] put limits of 0·95—1·05 on such slopes. Another necessary criterion is that the activity coefficient behaviour of the base under consideration should be the same as that of the bases used for the establishment of the acidity function scale. This latter criterion has rarely been substantiated in published studies on basicity constants and therefore we include the percentage (w/w) of H_2SO_4 at half protonation in the Table.

Since the slopes of $\log_{10}I$ *vs.* $-H_A$ are close to unity, one can reasonably state that the protonation equilibria of phenylureas are governed by the amide acidity function H_A and not by H_0, and it follows that any interpretation of kinetic data of ureas should be based on the H_A function.

(*Received, 5th April* 1972; *Com.* 551.)

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