Steroid–Acid Colour Reactions. Part I. Carbon-13 Nuclear Magnetic Resonance Spectra of Various Protonated Aliphatic Ketones and Their pK_{BH^+} Values

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The ^{13}C n.m.r. spectra of cyclopentanone, diethyl ketone, di-isopropyl ketone, cyclohexanone, dicyclopropyl ketone, cyclopropyl methyl ketone, and cyclohex-2-enone in sulphuric acid of various concentrations have been recorded. The maximum downfield change in the chemical shift, the apparent effect of complete protonation of the carbonyl group, is *ca.* 30 p.p.m. A plot of chemical shift against acidity shows that there is a gradual increase in apparent protonation but the form is not that of a normal titration curve. Solvation of the protonated ketone is suggested as explanation. A plot of log *I* against $-H_0$ has a slope of *ca.* 0.3. Values of H_0 at apparent half-protonation are reported and ^{13}C n.m.r. is shown to be an excellent method for the determination of the apparent basicity of a ketone. The results are treated by the method of Bunnett and Olsen and values of the thermodynamic pK_{BH^+} are obtained. The protonation of steroids is discussed.

COLOURS develop when certain steroids are dissolved in concentrated sulphuric acid and form the bases of many tests for their detection and estimation. The best known of these is the Liebermann–Burchard [1] reaction in which cholesterol is dissolved in a mixture of sulphuric acid and acetic anhydride to give an unstable blue solution. This has been used for the quantitative estimation of cholesterol for many years.[2] A modification by Zak *et al.*[3] includes ferric chloride in the reagent. When heated with concentrated sulphuric acid oestrogens develop an orange colour which turns pink on dilution and reheating.[4] Reaction with sulphuric acid at room temperature is used in the estimation of pregnane derivatives [5] and similar reactions are used for other classes of steroids. In spite of the widespread use of these procedures in clinical practice the chemistry involved has been little investigated. Details of previous work will be given as our studies of the different reactions are reported.

Sulphuric acid frequently effects protonation and carbonium ion formation [6] and it seems probable that these are the primary processes in the above reactions. Therefore, our first study has been an investigation of steroid carbonium ions. Jones,[7] who attempted to isolate and identify the coloured products of reaction, showed that numerous reactions subsequent to carbonium ion formation occur and so the task in hand is a formidable one but some progress has been made in favourable cases. Jones [8] has also shown that steroids without an hydroxy-group give simpler reactions.

A powerful tool for the study of carbonium ions is ^{13}C n.m.r.[9] and it has also been valuable in the elucidation of steroid structures.[10] Its use is, therefore, particularly appropriate for the study of steroid carbonium ions. As few such complex carbonium ions have been examined previously by ^{13}C n.m.r. it was decided to examine first the protonation of simple ketones.

There has been some previous work on this topic. The changes in chemical shift of acetone in sulphuric acid of various concentrations up to 63% have been reported by de Jeu.[11] Levy and Wilson [12] have shown that if the carbonyl chemical-shift of acetone is measured as a function of medium acidity, a titration curve is obtained and the value of H_0 at what is, apparently, half-protonation may be determined. Unfortunately no value has been published and experimental details are not available.[13] Therefore, this study comprises the protonation of simple ketones (diethyl ketone and di-isopropyl ketone), those where the positive charge can be delocalized (dicyclopropyl ketone and cyclopropyl methyl ketone), and those which are model compounds for different steroid rings (cyclohexanone, cyclopentanone, and cyclohex-2-enone). The results will not be presented in this order since, from a chemical point of view, a different pattern emerges.

RESULTS

Peak assignments are based, in general, on previous reports of the ^{13}C n.m.r., given in the first reference of each section.

(a) *Cyclopentanone.*[14]—Because of its high solubility this compound was examined throughout the complete range of sulphuric acid concentrations and the variation of chemical shift with acidity is given in Table 1. The chemical shift reflects the charge located on the carbon atom under consideration and is not a property of the whole molecule. The data show, therefore, the distribution of charge in the protonated molecule. Protonation has very little effect on C-3 and even C-2 is only slightly affected by the close

[1] C. Liebermann, *Ber.*, 1885, **18**, 1803; H. Buchard, *Chem. Zentr.*, 1890, **61**, 25.
[2] A. Grigant, *Compt. rend. Soc. Biol.*, 1910, **68**, 791.
[3] A. Zlatkis, B. Zak, and A. J. Boyle, *J. Lab. Clin. Med.*, 1953, **41**, 486; B. Zak, N. Moss, A. J. Boyle, and A. Zlatkis, *Analyt. Chem.*, 1954, **26**, 776.
[4] S. Kober, *Biochem. J.*, 1938, **32**, 357.
[5] N. B. Talbot, R. A. Barman, E. A. MacLachlan, and J. K. Wolfe, *J. Clin. Endocrinol.*, 1941, **1**, 668; A. I. Klopper, E. A. Michie, and J. B. Brown, *ibid.*, 1955, **12**, 209.
[6] D. Bethell and V. Gold, 'Carbonium Ions—an Introduction,' Academic Press, New York, 1967.
[7] H. A. Jones, *Nature*, 1967, **215**, 1381; H. A. Jones, *Canad. J. Spectroscopy*, 1971, **16**, 1; H. A. Jones and R. Hähnel, *Steroids*, 1969, **13**, 693.
[8] H. A. Jones, Ph.D. Thesis, University of Western Australia, 1968.
[9] G. A. Olah and R. D. Porter, *J. Amer. Chem. Soc.*, 1971, **93**, 6876.
[10] H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 7445.
[11] W. H. de Jeu, *J. Phys. Chem.*, 1970, **74**, 822.
[12] G. C. Levy and W. L. Wilson, unpublished results.
[13] G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley–Interscience, New York, 1972.
[14] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 1338.

proximity of the carbonium-ion centre. The maximum change in chemical shift, induced by the interplay of protonation and solvation effects, is *ca.* 30 p.p.m. on C-1 but only one tenth of that on C-2. The variation of chemical

TABLE 1

Variation of chemical shift with acidity for cyclopentanone

$[H_2SO_4]$/M	$-H_0$	C-1	C-2	C-3
0		230.9	40.7	25.1
1.81	0.76	230.8	40.8	25.1
3.29	1.49	231.1	40.9	25.1
5.83	2.63	232.9	40.9	25.1
8.07	3.58	234.7	41.0	25.1
10.01	4.68	236.4	41.3	25.1
11.40	5.48	239.7	41.4	25.1
14.09	7.08	245.4	42.0	25.3
15.78	8.08	250.0	42.5	25.5
17.22	9.12	254.6	43.1	25.4
18.66	10.48	259.5	43.6	25.5
$CDCl_3$		219.7	38.3	23.3

shift with acidity for C-1 has been plotted in Figure 1 and, although the plot has the general form of a titration curve, there are several significant differences. First, even in dilute acid where, based on the pK_a value, there should be no protonation, there is a definite downfield change in the chemical shift. Secondly, in more concentrated acid where protonation should occur, the slope is less than in a normal titration curve. This is reflected quantitatively in the value of m, the slope of plot of log I against $-H_0$ (see later). Thirdly, in this case the maximum chemical shift has been estimated by curved extrapolation, but the figure is quoted with confidence since the results may be analysed sensibly by the method of Bunnett and Olsen.[15] This estimated figure does not necessarily represent complete protonation of the carbonyl group since solvation effects are as important

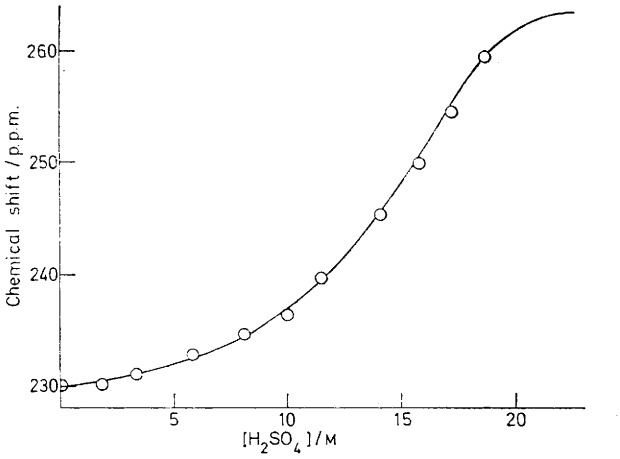


FIGURE 1 Variation of chemical shift of the carbonyl group with acid concentration for cyclopentanone

as protonation in affecting the chemical shift. This approach has been used previously with success [16] and the difficulty did not arise with other ketones, which also fit Bunnett–Olsen plots. Further analysis of the results will be delayed until other ketones have been considered.

(b) *Diethyl Ketone*.[17]—This ketone is not sufficiently soluble in dilute acid for the spectra to be recorded and considerable decomposition occurs if the recording time is prolonged. However, between 5.83 and 18.66M acid the chemical shift of the carbonyl group varies in a similar manner to that of cyclopentanone (Table 2). Only very small changes occur in the chemical shifts of the carbon atoms of the ethyl group. The chemical shift in aqueous solution was measured with a dilute solution of ketone; no decomposition occurs under these circumstances.

TABLE 2

Variation of chemical shift with acidity for the carbonyl group of various ketones

$[H_2SO_4]$/M	$-H_0$	Et_2CO	$Pr^i{}_2CO$	Cyclohexanone
0		222.9	229.1	223.8
5.83	2.63	224.6		224.2
8.07	3.58	225.1		225.7
10.01	4.68	227.1		228.0
11.40	5.48	229.7	233.8	232.2
14.09	7.08	235.2	240.2	238.5
15.78	8.08	242.2	247.6	246.3
17.22	9.12	249.7	255.1	249.9
18.66	10.48	252.1	257.8	251.5
$CDCl_3$		211.9	218.1	199.4

(c) *Di-isopropyl Ketone*.[17]—Solubility was a problem with this compound and spectra could not be obtained in acid less concentrated than 11.40M. Otherwise the results were similar to those of (a) and (b) (Table 2).

(d) *Cyclohexanone*.[14]—Apart from its surprisingly high solubility in acid as dilute as 5.83M, cyclohexanone showed no unusual features (Table 2). Only the carbon atom of the carbonyl group showed significant change in chemical shift.

(e) *Dicyclopropyl Ketone*.[18]—Here there is the possibility of delocalization of the positive charge over the cyclopropyl ring and this was found to be the case (Table 3). The

TABLE 3

Variation of chemical shift with acidity for ketone

$[H_2SO_4]$/M	$-H_0$	CO	CH	CH_2
0		218.3	23.0	13.6
1.81	0.76	219.0	22.8	13.7
5.83	2.63	221.4	23.0	14.0
8.07	3.58	224.5	23.0	15.3
10.01	4.68	229.4	23.4	18.3
11.40	5.48	234.3	23.9	21.8
14.09	7.08	236.7	24.5	24.0
15.78	8.08	237.4	24.9	24.9
17.22	9.12	237.6	25.1	25.3
18.66	10.48	237.9	25.3	25.7
$CDCl_3$		210.5	20.7	10.4

maximum change in the shift of the carbonyl group (19.7 p.p.m.) is smaller than with the ketones described previously. However, there is a substantial change in the shift of the methylene groups of the cyclopropyl ring (12.2 p.p.m.). On the other hand the methine carbon atom of the ring is much less affected by protonation (2.3 p.p.m.). Plots of chemical shift against acid concentration for both the carbonyl and methylene groups show the characteristically shallow slope and are not normal titration curves. The acid concentration at which apparent half-protonation occurs is not the same for the two groups; this matter will be discussed in detail later. In 15.78M sulphuric acid the shifts of all the carbon atoms of the cyclopropyl ring coincide (see

[15] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1899, 1917.

[16] P. Bonvicini, A. Levi, V. Lucchinic, G. Modena, and G. Scorrano, *J. Amer. Chem. Soc.*, 1973, **95**, 5960.

[17] L. M. Jackman and D. P. Kelly, *J. Chem. Soc.* (*B*), 1970, 102.

[18] J. B. Stothers and P. C. Lauterbur, *Canad. J. Chem.*, 1964, **42**, 1563.

Table 3). However, the off-resonance proton-decoupled spectrum converts this single peak into a quintuplet.

(f) *Cyclopropyl Methyl Ketone.*—This compound was examined in order that it might be compared with dicyclopropyl ketone. The results (Table 4) show that the positive

TABLE 4

Variation of chemical shift with acidity for cyclopropyl methyl ketone

$[H_2SO_4]$/M	$-H_0$	CO	CH	CH_2	CH_3
0		216.9	23.9	13.3	31.0
5.83	2.63	220.5	24.8	14.3	30.3
8.07	3.58	225.4	25.2	15.3	29.9
10.01	4.68	228.3	26.0	17.3	29.4
11.40	5.48	231.5	27.3	20.9	28.8
14.09	7.08	237.3	28.4	25.8	29.1
15.78	8.08	239.4	28.1	28.1	29.9
17.22	9.12	240.4	28.3	29.6	30.4
18.66	10.48	241.0	28.5	30.5	30.8
$CDCl_3$		208.7	21.2	10.6	30.0

charge is delocalized over the cyclopropyl group but the methyl group is only slightly affected by the proximity of the positive charge. This is what is expected from the results obtained with (b) and (e).

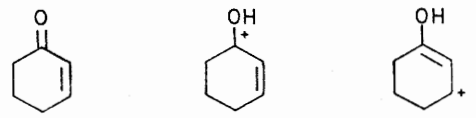
(g) *Cyclohex-2-enone.*[18,19]—This unsaturated ketone (I) is a model compound for the A ring of many steroids. It is soluble in dilute acid but in concentrated acid there is a fairly rapid reaction and a brown tar is formed. The data in Table 5 show that the charge resulting from protonation is extensively delocalized around the molecule. The shift on C-3 changes by a maximum of 29.1 p.p.m., while that of C-1 by only 12.0 p.p.m. The change of C-2 is an *upfield* one of 3.3 p.p.m. These figures demonstrate that (II) and (III) are

TABLE 5

Variation of chemical shift with acidity for cyclohex-2-enone

$[H_2SO_4]$/M	$-H_0$	C-1	C-2	C-3
0		207.7	130.5	158.6
1.81	0.76	207.8	130.5	158.9
3.29	1.49	208.1	130.2	159.4
5.83	2.63	209.3	130.1	161.0
8.07	3.58	210.7	129.7	163.3
10.01	4.68	213.6	129.0	168.8
11.40	5.48	216.4	128.1	176.1
14.90	7.08	218.6	127.6	182.8
15.78	8.08	219.1	127.3	186.3
17.22	9.12	219.5	127.2	187.1
$CDCl_3$		199.4	129.9	150.5

the two canonical forms of the carbonium ion and (III) appears to be the more important one. However, the acid



(I) (II) (III)

concentration at apparent half-protonation is different for C-1 and C-3 and so the situation cannot be as simple as suggested above. The matter will be discussed in detail later.

[19] D. H. Marr and J. B. Stothers, *Canad. J. Chem.*, 1965, **43**, 596.
[20] E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 223.
[21] L. A. Flexser, L. P. Hammett, and A. Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103; R. Stewart and K. Yates, *ibid.*, 1958, **80**, 6355; R. Stewart and M. R. Granger, *Canad. J. Chem.*, 1961, **39**, 2508; K. Yates and R. Stewart, *ibid.*, 1959, **37**, 664.
[22] H. J. Campbell and J. J. Edwards, *Canad. J. Chem.*, 1960, **38**, 2109.

DISCUSSION

The most obvious value of this work is that it permits the quantitative study of ketones as weak bases. Earlier work on this subject has been reviewed by Arnett.[20] Measurement of changes in the visible and u.v. spectra is the usual method of measuring ketone basicity [21] but the results can be rendered meaningless by small traces of impurity and difficulties may arise in separating the effects of protonation and hydrogen bonding on the observed spectra.[22] The advantages of an n.m.r. method have been reviewed by Levy *et al.*[23] and these workers used proton n.m.r. to measure the basicity of a number of ketones. ^{13}C N.m.r. is even more powerful since it measures directly changes of charge on the carbonyl group, rather than changes in the deshielding of the protons on the neighbouring carbon atom.

Interpreting the results of basicity measurements of ketones is not simple. Ketones do not behave as true Hammett bases [24] and thermodynamically meaningful pK_{BH^+} values cannot be obtained directly. The value of H_0 at half-protonation, which is what is reported by Levy *et al.*,[23] allows the basicities of a series of ketones to be compared. An even simpler procedure is to report the acid molarity at half-protonation since H_0 values have no particular significance in ketone protonation.

The most significant result obtained in this study is that a plot of chemical shift against acid molarity does not have the features of a normal titration curve in that the curve is too shallow (Figure 1). The results of Levy *et al.*[23] using proton n.m.r. show the same effect for some ketones. Significantly they found that the use of solvents containing trifluoroacetic acid gave curves which were more nearly titration curves. This suggests that it is aqueous sulphuric acid, as well as the ketone, which behave in an anomalous manner. All the ketones studied in the present work were nonaromatic and they protonate less readily than aromatic ketones; this is shown by the fact that they do not follow the benzophenone acidity scale proposed by Bonner and Phillips.[25] In aromatic ketones the positive charge resulting from protonation may be delocalized over the aromatic ring [26] and the inability of aliphatic ketones to do this may partly explain their behaviour as bases. If delocalization cannot occur in any other way, solvation of the localized carbonium ion is of paramount importance. The availability of water molecules in the solvent is as important as the protonating ability of the acidic species in producing a carbonium ion. As the acidity of sulphuric acid increases, so the activity of water (which is a crude measure of solvating power) decreases.[27] It is thus

[23] G. C. Levy, J. D. Cargioli, and W. Racela, *J. Amer. Chem. Soc.*, 1970, **92**, 6238.
[24] C. C. Greig and C. D. Johnson, *J. Amer. Chem. Soc.*, 1968, **90**, 6354.
[25] T. G. Bonner and J. Phillips, *J. Chem. Soc.* (*B*), 1966, 650.
[26] N. K. Skvortsov, V. P. Lizinea, A. U. Stepanyants, G. F. Tereshchenko, and B. I. Ionin, *Zhur. obshchei Khim.*, 1974, **44**, 2293.
[27] J. E. Kunzler and W. F. Giaque, *J. Amer. Chem. Soc.*, 1952, **74**, 3472.

possible to understand, in a qualitative manner, the behaviour of aliphatic ketones in sulphuric acid. At concentrations sufficiently acid to protonate the ketone there is insufficient water to solvate completely the resulting carbonium ion. Acidity appears to be the stronger factor, but protonation in dilute acid is enhanced owing to the high water activity and the result is a shallow increase in protonation with increasing acid concentration.

Values of acid molarity and H_0 at half-protonation are given in Table 6. The error in both is *ca.* ± 0.2 units.

TABLE 6

Acid–base equilibria of various ketones

		$[H_2SO_4]_{\frac{1}{2}}$/M	$(H_0)_{\frac{1}{2}}$	m	pK_{BH^+}	ϕ
(a) Cyclopentanone	C=O	14.5	−7.2	0.25	−2.3	0.85
(b) Diethyl ketone	C=O	14.9	−7.4	0.30	−2.9	0.77
(c) Di-isopropyl ketone	C=O	15.1	−7.6	0.36	−3.5	0.66
(d) Cyclohexanone	C=O	13.6	−6.6	0.36	−3.1	0.67
(e) Dicyclopropyl ketone	C=O	9.3	−4.4	0.42	−2.4	0.63
	CH_2	10.5	−5.4	0.39	−2.6	0.61
(f) Cyclopropyl methyl ketone	C=O	10.2	−4.7	0.33	−2.3	0.72
	CH_2	12.1	−6.0	0.35	−2.7	0.72
(g) Cyclohex-2-enone	C=O	9.9	−4.8	0.39	−2.5	0.62
	CH (C-3)	11.3	−5.2	0.42	−2.9	0.63

For acetone previously reported values of $(H_0)_{\frac{1}{2}}$ are: −7.2 (u.v. spectroscopy),[22] −7.2 (Raman spectroscopy),[28] −7.5 (proton n.m.r.),[23] and −7.8 (proton n.m.r.).[29] The values obtained, therefore, for ketones (a)—(d) are reasonable ones. It is surprising to find that cyclohexanone is significantly more basic than the others. Possibly puckering of the cyclohexane ring permits, for steric reasons, better solvation of the carbonium-ion centre.

Ketones (e), (f), and (g), where delocalization of the charge is possible, are more basic. In these cases $(H_2SO_4)_{\frac{1}{2}}$ and $(H_0)_{\frac{1}{2}}$ may be determined from the chemical shifts of two carbon atoms and the values differ markedly, by 1.3 H_0 units in the case of cyclopropyl methyl ketone. The previously determined value of $(H_0)_{\frac{1}{2}}$ for this compound is −5.9,[23,29] which agrees with that calculated from the shifts of the methylene groups but differs from that of the carbonyl group. This is reasonable since the previously reported value was determined by measurement of the proton n.m.r. It is possible that different basicities for the same molecule could be the result of protonation of a site other than the carbonyl group; edge protonation with (e) and (f) and at C-3 in (g). However, if only a monoprotonated species is formed then the basicity of the ketone would be that of the more basic site. Diprotonation could occur only at acidities much higher than those examined. A more likely explanation of the apparently differing basicities is differential solvation, which will be discussed in detail after the Bunnett–Olsen treatment of the results has been described.

If ketones were Hammett bases then a plot of log I, where I is the ionization ratio $[BH^+]/[B]$, against $-H_0$ should be linear with a slope (m) of unity. I Is evaluated from equation (1), where $\Delta\nu$ is the chemical shift of the partially protonated compound. Values of m for ketones

$$I = (\Delta\nu - \Delta\nu_B)/(\Delta\nu_{BH^+} - \Delta\nu) \quad (1)$$

(a)—(g) are given in Table 6; they vary from 0.25 to 0.42, indicating how remote the behaviour of ketones is from that of a Hammett base. The values of m appear to vary in a random manner.

Thermodynamic pK_{BH^+} values may be calculated from the data by the treatment of Bunnett and Olsen.[15] A

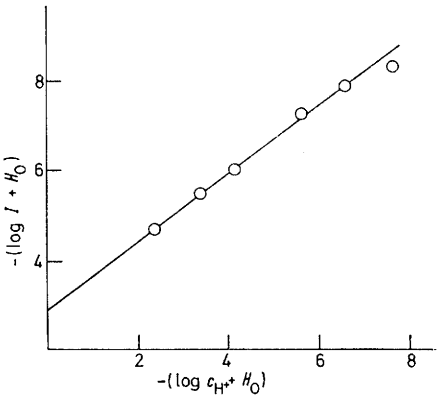


FIGURE 2 Bunnett–Olsen plot for the protonation of diethyl ketone

parameter ϕ may also be calculated from equation (2) which gives information concerning solvation require-

$$\log I + H_0 = \phi(H_0 + \log c_{H^+}) + pK_{BH^+} \quad (2)$$

ments of the protonation equilibrium.[30] For example, Scorrano *et al.*[31] found that ϕ values for the protonation of ethers and sulphides are *ca.* +0.8 and *ca.* −0.3 respectively, indicating that sulphonium ions are less solvated than oxonium ions. The presence of the large and polarizable sulphur atom makes the dispersion of the positive charge occur more readily in R_2SH^+ than in R_2OH^+ and hence solvation is less important in the former. Values of ϕ and pK_{BH^+} for ketones (a)—(g) are given in Table 6 and a typical plot in Figure 2. The values of ϕ are all *ca.* 0.7 and confirm the highly significant role of solvation in stabilizing the protonated form of a ketone. It is as great as that of an oxonium ion.

Within the group of ketones examined there is a smaller spread in the values of pK_{BH^+} than of $(H_0)_{\frac{1}{2}}$. This means that in dilute solution, where solvation is no problem, ketones have similar basicities but in concentrated acid, where less water is available for solvation, ketones show

[28] N. C. Deno and M. J. Wisotsky, *J. Amer. Chem. Soc.*, 1963, **85**, 1735.

[29] A. Levi, G. Modena, and G. Scorrano, *J. Amer. Chem. Soc.*, 1974, **96**, 6585.

[30] D. J. Lee and R. Cameron, *J. Amer. Chem. Soc.*, 1971, **93**, 4724.

[31] R. Curci, F. Di Furia, A. Levi, V. Lucchini, and G. Scorrano, *J.C.S. Perkin II*, 1975, 341.

greater variation in basicity. Those which can delocalize charge by some other mechanism become relatively more basic. The apparently different basicities of different sites in certain ketones partially disappear when the pK_{BH^+} values are examined and this effect can be explained by solvation. Charge is delocalized over the molecule to an extent which is governed by the molecular structure and the possibility of solvation of the various charged centres. Steric factors will be important in the latter. In concentrated acid, as solvation becomes more difficult, the distribution of charge around the molecule will change, increasing most where solvation is easiest. The changing distribution of charge as the acidity is increased will give rise to distorted ' titration ' curves and, hence, apparently differing basicities. A description of the behaviour of a weak base like a ketone in concentrated acid needs a knowledge of solvation requirements as well as the thermodynamic pK_{BH^+}.

The above analysis may appear remote from the simple colorimetric tests for steroids employed in clinical chemistry but the following paper shows that similar considerations may be applied to the protonation of a number of steroids.

EXPERIMENTAL

Materials.—All the ketones were commercial samples purified by distillation before use. AnalaR sulphuric acid was diluted and standardized by density measurements. The H_0 values were obtained by interpolation of published data.[32]

Spectral Measurements.—Spectra were recorded on a Varian CFT-20 spectrophotometer with a sample temperature of *ca.* 40 °C. The samples were 1—2M in ketone. Chemical shifts in sulphuric acid were measured relative to the sodium salt of 3-(trimethylsilyl) propanesulphonic acid and those in deuteriochloroform relative to tetramethylsilane.

Professor P. A. H. Wyatt is thanked for helpful discussion and Melanja Smith for recording all the spectra.

[5/1806 *Received*, 18*th September*, 1975]

[32] C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, 1969, **91**, 6654.