Quantitative Aspects of Lewis Acidity. Part XIII.[1] Basicity of Substituted Benzamides towards Metal Halides. The Validity of Nuclear Magnetic Resonance Chemical Shifts as Measures of Lewis Acid Strength [2]

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$ZnCl_2$, $ZnBr_2$, BF_3, $GaCl_3$, $GaBr_3$, $PhSnCl_3$, $SnCl_4$, $AlCl_3$, $SbCl_3$, and $AsCl_3$ form 1 :1-adducts with substituted benzamides in diethyl ether or in tetrahydrofuran. The values of K, the equilibrium constant for adduct formation in diethyl ether, follow the sequence $AlCl_3 > SnCl_4 > GaCl_3 \simeq GaBr_3 > ZnCl_2 \simeq ZnBr_2 \geqslant BF_3 > PhSnCl_3 > SbCl_3 > AsCl_3$. The K values are larger in diethyl ether than in tetrahydrofuran. It is shown that the carbonyl oxygen atom of the benzamide is the donor atom. It is also demonstrated that neither standard heats of formation of the adducts nor the resulting ^1H n.m.r. chemical shifts of the N–H protons are reliable guides to the relative acidities of the covalent halides. The relative basicity of benzamides and anilines towards metal halides is very different to their relative basicity towards the proton in water. The pK_a value of 2-methylbenzamide is $-1{\cdot}88$ and molecular weight determinations show that gallium chloride is monomeric in ether.

THE majority of earlier quantitative studies of metal halide acid–organic base equilibria have involved nitrogen bases. Few quantitative studies with oxygen bases have been reported. In one such study the

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[1] Part XII, A. Mohammad and D. P. N. Satchell, *J. Chem. Soc. (B)*, 1968, 331.

[2] Preliminary communication, D. P. N. Satchell and R. S. Satchell, *Chem. Comm.*, 1969, 110.

formation of 1 : 1-adducts between boron trifluoride and substituted benzamides in tetrahydrofuran solution was investigated.[3] The pK values were found to correlate well with σ substituent parameters. No other acids were investigated. A few equilibrium constants for 1 : 1-adduct formation between ketones and metal halides in diethyl ether solution have been reported.[4,5] The results suggested that for ketones and anilines with comparable pK_a values (proton basicities), the former are much more basic than the latter towards metal halides in diethyl ether.[4,6] To investigate these matters further we have now measured the equilibrium constants for 1 : 1-adduct formation between substituted benzamides and a series of metal halides in diethyl ether solution. Some measurements have also been made using tetrahydrofuran as solvent over a range of temperatures to obtain values for ΔH^0 and ΔS^0.

At the same time we have tested the assumption[7] that n.m.r. chemical shifts may be used to obtain sequences of relative Lewis acidity. In no previous study has an attempt been made to correlate n.m.r. data with equilibrium constants obtained under similar conditions.

EXPERIMENTAL

Materials.—' Anhydrous ' diethyl ether was purified by methods previously used in this laboratory.[8] Tetrahydrofuran was purified by Ellul and Moodie's method,[3] except that after the final distillation from lithium aluminium hydride, the flask containing the distillate was placed immediately in a dry box, and no molecular sieve was added. The majority of the bases were commercial samples recrystallised to constant m.p. 3,5-Dinitro- and 3-nitro-benzamide were prepared by reaction of the relevant benzoyl chloride with ammonia, and *N*-methylbenzamide by the reaction of benzoyl chloride with methylamine. The products were recrystallised to constant m.p. All m.p.s agreed with literature values. Boron trifluoride–diethyl ether,[9] antimony trichloride,[8] gallium chloride,[10] gallium bromide,[10] stannic chloride,[11] zinc chloride,[12] and zinc bromide[12] were purified by established methods. Arsenic trichloride (99·999% purity) was used without further purification. Aluminium chloride was repeatedly sublimed, very slowly, at 10 mmHg until a white crystalline solid was obtained. Trichlorophenyltin was prepared by Luijten and van der Kerk's method.[13] It had b.p. 76° at 0·2 mmHg. Analysis of the product for chloride by conductometric titration with silver nitrate gave the purity as 99·9%. All manipulations with the purified metal halides and their solutions were performed in a dry-box.

pK_a *of* 2-*Methylbenzamide*.—The u.v.-visible spectra of a constant total concentration of 2-methylbenzamide in sulphuric acid–water mixtures showed no isosbestic point. This is typical of the behaviour of benzamides in sulphuric acid.[14] It has been found for other benzamides that the spectra improve in aqueous perchloric acid.[15] The spectra of 2-methylbenzamide in perchloric acid–water mixtures showed a reasonable isosbestic point at 227 nm. The majority of the spectra were, however, shifted slightly (0·2—5 nm) to improve this isosbestic point, and so minimise the medium effect which underlies its otherwise poor quality.[14,15] The absorbance at the maximum of the absorption band of the protonated base also increases with acid concentration, even after the base is completely protonated. This means that D_∞, the absorbance corresponding to completely protonated base at any wavelength, cannot be obtained directly. D_∞ was therefore found from a plot of $(D - D_0)/h_0$ against D, where D_0 and D were the absorbances observed at some chosen wavelength in the absence of acid, and in the presence of acid, respectively and $h_0 = -\text{antilog}\ H_0$. For a well-behaved system it can be shown that such a plot will be rectilinear and give D_∞ as the intercept on the D axis. In the present case, the plot is rectilinear until the base is *ca.* 80% protonated and D_∞ was obtained by extrapolation. With D_∞ thus obtained, a plot of $\log\,[(D - D_0)/(D_\infty - D)]$ ($= \log\,[\mathrm{BH^+}]/[\mathrm{B}]$) against H_0 is also rectilinear with a slope 1·07. This is a very different result from the behaviour of benzamides in sulphuric acid, in which their protonation generally does not follow the H_0 acidity scale, but rather the H_A scale.[16] However, the protonation of 2-methylbenzamide in sulphuric acid has been reported (i) not to follow the H_A acidity scale[16] and (ii) to show a reasonable dependence on H_0.[17] Also the protonation of benzamides has been reported to follow the H_0 acidity scale more closely in perchloric acid than in sulphuric acid.[18] Since our slope in perchloric acid is close to unity, the pK_a value calculated with the aid of H_0 is considered to be reliable. A value of $-1·88$ was obtained for the pK_a of 2-methylbenzamide at two different wavelengths. This value agrees well with an earlier approximate value[16] of $-1·8$.

Reaction Mixtures.—These were prepared and analysed by methods we have used previously.[1,8-10]

Equilibrium Measurements.—Equilibrium constants,* K = [Adduct]/[Base][Acid], for reaction (1) were determined as before.[9] The absorbance changes that accompany

$$\mathrm{PhCONH_2 + MX_nS_y \rightleftharpoons PhCONH_2MX_nS_{y-1} + S} \qquad (1)$$

adduct formation for 4-nitrobenzamide are very small. The accuracy of the measurements was here improved by using a Unicam SP800 spectrophotometer fitted with an 8P850 scale expansion accessory in conjunction with a Kent recorder.

The Adducts' U.v.–Visible Spectra.—The spectra of solutions containing a fixed amount of base and varying

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* The solvent concentration is omitted conventionally from the expression for K.

[3] B. M. J. Ellul and R. B. Moodie, *J. Chem. Soc.* (*B*), 1967, 253.

[4] A. Mohammad, D. P. N. Satchell, and R. S. Satchell, *J. Chem. Soc.* (*B*), 1967, 723.

[5] A. Mohammad, D. P. N. Satchell, and R. S. Satchell, *J. Chem. Soc.* (*B*), 1967, 727.

[6] D. P. N. Satchell and R. S. Satchell, *Chem. Rev.*, 1969, **69**, 251.

[7] J. M. Miller and M. Onyszchuk, *Canad. J. Chem.*, 1964, **42**, 1518.

[8] R. M. Evans and R. S. Satchell, *J. Chem. Soc.* (*B*), 1970, 1667.

[9] R. S. Satchell and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1967, 36.

[10] A. Mohammad and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1967, 403.

[11] R. M. Evans and R. S. Satchell, *J. Chem. Soc.* (*B*), 1970, 300.

[12] R. S. Satchell, *J. Chem. Soc.*, 1964, 5464.

[13] J. A. Luijten and G. J. M. Van Der Kerke, ' Investigations in the Field of Organotin Chemistry,' Tin Research Institute, Greenford, Middlesex, 1955.

[14] K. Yates and J. B. Stevens, *Canad. J. Chem.*, 1964, **42**, 1957.

[15] R. B. Moodie, P. D. Wale, and T. J. Whaite, *J. Chem. Soc.*, 1963, 4273; R. B. Homer and R. B. Moodie, *ibid.*, p. 4377.

[16] K. Yates and J. B. Stevens, *Canad. J. Chem.*, 1965, **43**, 529.

[17] K. Yates and B. F. Scott, *Canad. J. Chem.*, 1963, **41**, 2320.

[18] K. Yates and H. Wai, *Canad. J. Chem.*, 1965, **43**, 2131.

amounts of metal halide were recorded as soon as possible after mixing. The spectra were stable, and the majority showed good isosbestic points. Thus only one adduct is formed in these systems.

^{1}H *N.m.r. Spectra.*—The n.m.r. spectra of solutions of a number of substituted benzamides with various metal halides in diethyl ether were determined as before.[2]

Molecular Weight.—The molecular weight of gallium chloride in diethyl ether solution was determined over a range of concentrations (0·01—0·10 mol dm^{-3}) with a Gallenkamp semimicro ebulliometer. Naphthalene was used to determine the ebullioscopic constant. Gallium chloride is found to be accurately monomeric (Found: *M*, 180. Calc. for $GaCl_3$: *M*, 176).

RESULTS AND DISCUSSION

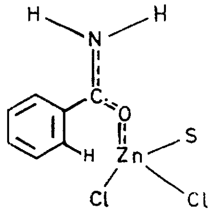
U.v. and Visible Spectral Effects on Adduct Formation.—Generally, as for protonation,[14] adduct formation leads to the removal of the free base's longest wavelength absorption band, and a new band, shifted 2—16 nm to longer wavelengths and of higher intensity, appears which is characteristic of the adduct. In one case (4-nitrobenzamide) the new band occurs at a slightly shorter wavelength. The spectral effects in tetrahydrofuran solution are virtually identical with those in diethyl ether. Since the spectral effects on adduct formation with metal halides are very similar to those observed on protonation of the benzamides, it is concluded that the same co-ordination site is involved in the two cases.

Site of Co-ordination, ^{1}H *N.m.r. Spectra, and Adduct Geometry.*—It is conceivable that either nitrogen or oxygen could act as the donor atom in substituted benzamides. However, it has been shown that protonation in concentrated acid occurs at oxygen.[19] Also n.m.r. spectroscopy has shown that in amides there is restricted rotation about the carbon–nitrogen bond due to its partial double bond character.[20,21]

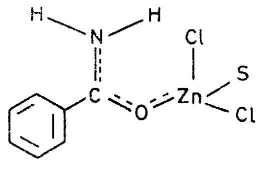
Kuhn and McIntyre[22] found two methyl proton signals in the n.m.r. spectra of a number of metal halide adducts of dimethylformamide in 2-nitropropane or in methylene dichloride solution. The presence of the two signals, one for each methyl group, shows clearly that in these adducts the metal halide is co-ordinated to the oxygen atom: co-ordination to the nitrogen atom would have destroyed the carbon–nitrogen double bond character, and rendered the methyl groups positionally equivalent. In the same way the majority of our n.m.r. spectra of the adducts of primary amides in the presence of an excess of metal halide contained two broad N–H peaks. Integration of the spectra confirmed that the two peaks were of equal size, and also gave the correct ratio for the N–H protons to the aromatic C–H protons. In a few cases, only one N–H peak was detected separate from the aromatic C–H peaks. In these cases integration showed that the second N–H peak was under the aromatic C–H peaks.

It is concluded that in these adducts in diethyl ether the metal halides are co-ordinated to the carbonyl oxygen atom.

We have previously argued that there may be a double bond between the metal and the donor atom *in* metal halide-*O*-base adducts.[4,6] If the N–C, C–O, and O–metal bonds all have some double bond character then, for say zinc chloride, it is likely that the nitrogen, carbon, oxygen, and zinc atoms will be coplanar. In this situation two structures are possible so far as the configuration about the C–O bond is concerned: the zinc atom can take up a position either *trans* (I) or *cis* (II) to the amino-group. Of these two possibilities, structure (I) is unlikely owing to steric interference between a halogen atom and the *ortho*-hydrogen atom of the benzamide. Such steric interference would be greatly magnified by substitution of a methyl group in the *ortho*-position, but our equilibrium studies (see below) show no evidence of such a steric effect. We therefore prefer structure (II) to structure (I). Moreover, if both *cis*- and *trans*-structures were present in significant amounts in adducts of primary amides, then four and not two N–H signals should be found in the n.m.r. spectra.



(I)



(II)

Accepting structure (II) for the geometry about the C–O bond, there remains the question of isomerism about the C–N bond for *N*-substituted amides, *e.g.* *N*-methylbenzamide. Again, if the methyl group can take up positions both *cis* and *trans* to the carbonyl oxygen atom then the n.m.r. spectra of its adducts should contain two N–Me and two N–H signals, each N–Me signal being split as a doublet. However, such spectra always contain only one N–Me signal (doublet) and one N–H signal (which is too broad to permit detection of any fine structure). This result makes it clear that not only is just one configuration greatly preferred about the C–O bond, but also about the C–N bond. This configuration is likely to be that with the methyl group *trans* to the carbonyl oxygen atom (III), since otherwise serious steric interference with a halogen atom is incurred. Structure (III) may also be stabilised by hydrogen-bonding, especially when BF_3 is involved [(IV)]. Free *N*-methylbenzamide, however, prefers the *cis* configuration,[23] and if this has to change to *trans* on adduct formation with covalent halides the relative

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[19] T. Birchall and R. J. Gillespie, *Canad. J. Chem.*, 1963, **41**, 148, 2642.

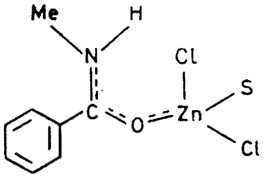
[20] W. D. Phillips, *J. Chem. Phys.*, 1955, **23**, 1363.

[21] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.

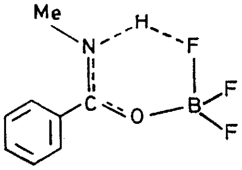
[22] R. J. Kuhn and J. S. McIntyre, *Canad. J. Chem.*, 1965, **43**, 375.

[23] J. E. Worsham and M. E. Hobbs, *J. Amer. Chem. Soc.*, 1954, **76**, 206.

reluctance of the N-methyl derivative to form such adducts compared with benzamide is understandable (*see below*).



(III)



(IV)

Equilibrium Constants.—Our pK values are summarised in Tables 1 and 2. As in our earlier studies with anilines,[6,9,10] we find a rectilinear relationship between the pK value in ether and the pK_a value of the base in water. The relevant correlation equations are p$K = -0{\cdot}79$p$K_a - 4{\cdot}69$ for $ZnCl_2$ and $ZnBr_2$, p$K = -1{\cdot}11$p$K_a - 5{\cdot}54$ for BF_3, and p$K = -1{\cdot}55$p$K_a - 6{\cdot}51$ for $PhSnCl_3$. For $GaBr_3$ an approximate equation based on two bases of Δp$K_a = 0{\cdot}9$ is p$K = -1{\cdot}20$p$K_a - 6{\cdot}36$. In Table 1 pK values calculated using these equations are compared with the observed values. For 2-methylbenzamide with $ZnCl_2$, or with BF_3, the agreement between the observed and calculated values is good. Thus the 2-methyl group does not lead to significant steric hindrance in the metal halide adducts. The probable reasons for this are discussed in the foregoing section. On the other hand, the calculated pK values for N-methylbenzamide are much more negative than the observed values. Thus K is smaller than expected; the probable reasons for this have also been discussed above.

TABLE 1

pK Values for 1 : 1-adduct formation between metal halides and substituted benzamides in diethyl ether at 25°

K_a is the acid dissociation constant of the protonated base in water at 25°. The pK values in parentheses are values calculated using the pK/pK_a correlation equations given in the text. Units of K are mol^{-1} dm^3

Benzamide derivative	pK_a	$ZnCl_2$	$ZnBr_2$	BF_3	$GaCl_3$	$GaBr_3$	$PhSnCl_3$	$SnCl_4$	$AlCl_3$	$SbCl_3$	$AsCl_3$
4-MeO	−1·80	−3·56 (−3·27)									
2-Me	−1·88	−3·14 (−3·20)		−3·4 (−3·45)							
4-Me	−2·01	−3·15 (−3·10)	−3·17								
N-Me	−2·13	−2·34 (−3·01)		−1·25 (−3·18)	−3·0						
	−2·16	−2·96 (−2·98)		−3·1 (−3·14)							
4-F	−2·24	−2·83 (−2·92)									
3-MeO	−2·35	−2·94 (−2·83)	−2·94	−2·93 (−2·93)			−2·87 (−2·87)			−1·76	−0·8
4-Cl	−2·47	−2·72 (−2·74)	−2·56	−2·87 (−2·80)		−3·40					
3-Br	−2·75	−2·52 (−2·52)		−2·53 (−2·49)			−2·23 (−2·25)				
3-NO_2	−3·07	−2·21 (−2·26)		−2·14 (−2·13)	−2·62		−1·75 (−1·75)				
4-NO_2	−3·23	−2·17 (−2·14)	−2·17	−1·86 (−1·95)	−2·53	−2·49	−1·53 * (−1·50)	−2·80	−3·03 *		

* Values at 21°. The low ΔH^0 values in tetrahydrofuran suggest at 25° these values would be *ca.* 0·03 units more positive.

TABLE 2

pK, ΔH^0, and ΔS^0 values for 1 : 1-adduct formation between metal halides and substituted benzamides in tetrahydrofuran

Units of K, ΔH^0, and ΔS^0 are mol^{-1} dm^3, kcal mol^{-1}, and cal mol^{-1} K^{-1} respectively

Benzamide derivative	Acid	pK at 298 K	ΔH^0	ΔS^0 *
4-MeO	$ZnCl_2$	−1·75	−3·6 ± 0·1	−4·0 ± 0·3
3-MeO	$ZnCl_2$	−1·36	−3·0 ± 0·1	−3·7 ± 0·3
3-MeO	$SnCl_4$	−2·16	−3·8 ± 0·1	−2·8 ± 0·3

* The values of ΔS^0 with the solvent concentration included in the expression for K are 5·0 units more positive.

Comparison of the present data with those previously obtained for metal halide–substituted aniline equilibria [6,9,10] reveals that anilines and benzamides of similar pK_a lead to very different K values with any given metal halide. Indeed the benzamides are found to be 10^4—10^6 fold more basic than expected compared with the anilines. Similar results [4,5,24] have been obtained in other comparisons of oxygen and nitrogen bases in aprotic solvents, and we have discussed the possible origins of these effects in earlier papers.[4,5,25]

Solvent Effects.—A comparison of the results in Table 1 with those in Table 2, and also of our results for BF_3 in ether with those of Ellul and Moodie for BF_3 in tetrahydrofuran,[3] shows that for $ZnCl_2$, $SnCl_4$, and BF_3 K is 30—60 times greater in diethyl ether than in tetrahydrofuran. This is a sensible result, since tetrahydrofuran is a stronger base than diethyl ether and will therefore be expected to lead to a lower level of acidity. Thus the value of K for reaction (2) in the

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[24] R. W. Taft, D. Gurka, L. Joris, P. von R. Schleyer, and J. W. Rakshys, *J. Amer. Chem. Soc.*, 1969, **91**, 4801.

[25] D. P. N. Satchell and R. S. Satchell, *Quart. Rev.*, 1971, **25**, 171.

liquid state[26] is 32, and in benzene solution tetrahydrofuran is much more basic than diethyl ether towards $SnCl_4$.[27]

$$Et_2O{:}BF_3 + THF \rightleftharpoons Et_2O + THF{:}BF_3 \quad (2)$$

Relative Acidities of Covalent Metal Halides.—The values of K for 1 : 1-adduct formation with benzamides in ether follow the sequence $AlCl_3 > SnCl_4 > GaCl_3 \simeq GaBr_3 > ZnCl_2 \simeq ZnBr_2 \geqslant BF_3 > PhSnCl_3 > SbCl_3 > AsCl_3$ (see Table 1). Towards substituted anilines in ether the sequence is[1,6,9,10] $BF_3 \simeq AlCl_3 \simeq GaBr_3 \simeq GaCl_3 \simeq SnCl_4 > ZnCl_2 \simeq ZnBr_2 > PhSnCl_3 > SbCl_3$, and towards the ketone perinaphthenone[4] it is $GaCl_3 \gg SnCl_4 > ZnBr_2 > ZnCl_2 > PhSnCl_3 > BF_3$. In general these lists are very similar, with benzamides distinguishing between the acidity of the acids more clearly than the anilines. The much lower position of BF_3 in the ketone and benzamide lists than in the aniline list, supports the view that some oxygen–metal double bonding is involved in most of the adducts, in which, owing to a lack of suitable orbitals, boron is unable to participate.

ΔH^0 *and* ΔS^0 *Values.*—Heats of adduct formation with a standard base in some solvent have often been used in the past to compare Lewis acidities, especially when the relevant equilibrium constants were not so easily determined. The (limited) experiments reported in Table 2 show, however, that on adduct formation the changes in ΔS^0 can be as significant as the changes in ΔH^0, so that changes in $K(\Delta G^0)$ will not necessarily parallel changes in ΔH^0. The very small ΔH^0 and ΔS^0 values found for the present systems can be attributed to the relatively great basic strength of the solvent tetrahydrofuran, and to its being an oxygen base like the (standard) amide bases used. Thus the bonding in the solvent–metal halide adducts may well be very similar to that in the benzamide adducts, so leading to the small values for ΔH^0 and ΔS^0.

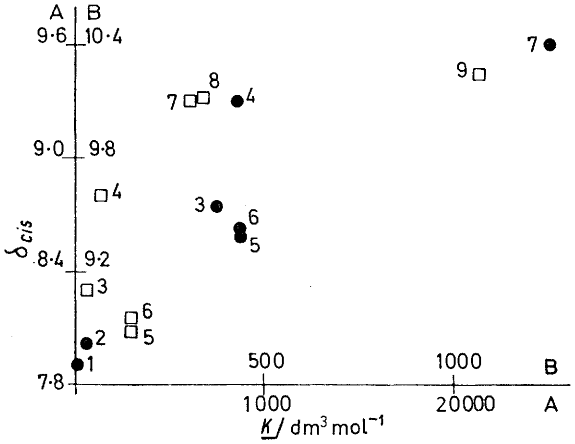
N.m.r. Chemical Shifts as a Measure of Acidity.—The chemical shifts (from an internal reference of tetramethylsilane) of the NH protons in the adducts of 3-methoxy- and 4-nitro-benzamide with metal halides are given in Table 3. These results show that the chemical shift, δ, generally becomes more negative the stronger the Lewis acid. Preliminary results[2] using a few acids suggested that δ was, in fact, rectilinearly related to K, but the results now available with a wider range of acids show that this is not the case (Figure).

TABLE 3

Chemical shifts and equilibrium constants

δ = chemical shift in p.p.m. from internal Me_4Si; δ_{cis} and δ_{trans} represent respectively the shifts for NH protons *cis* and *trans* to the carbonyl group.[19, 22] Values of K are taken from Table 1

Acid	Benzamide	K	$-\delta_{cis}$	$-\delta_{trans}$
$PhSnCl_3$	3-MeO	740	8·74	7·91
$PhSnCl_3$	4-NO_2	34	9·10	8·62
$AlCl_3$	4-NO_2	1070	10·25	9·83



Plot of δ_{cis} against K: A, ●, 3-methoxybenzamide; B, ☐, 4-nitrobenzamide: 1, $AsCl_3$; 2, $SbCl_3$; 3, $PhSnCl_3$; **4**, BF_3; 5, $ZnBr_2$; 6, $ZnCl_2$; 7, $GaBr_3$; 8, $GaCl_3$; 9, $AlCl_3$

The sequence of chemical shifts is not even quite the same as the sequence of K values. It is therefore concluded, as for measurements of heats of reaction, that measurements of chemical shifts are unlikely to provide a reliable shortcut to relative acidities.

[4/1946 *Received, 23rd September*, 1974]

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[26] M. Okada, K. Sugama, and Y. Yamashita, *Tetrahedron Letters*, 1965, **28**, 2329.

[27] J. J. Myher and K. E. Russell, *Canad. J. Chem.*, 1964, **42**, 1555.