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(12) A portion of this problem was completed while J. W. Wheeler was a Special Fellow in the Laboratory of Chemistry, National Heart and Lung Institute, Bethesda, Md. We thank H. M. Fales for facilities, for continuing access to the gc-mass spectrometer, and for suggesting the second synthesis of I. We also thank the National Science Foundation COS-IPD Program and the National Institutes of Health MSBS Program for partial support.

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Acidities of Carbon Acids. IV.[1] Kinetic *vs.* Equilibrium Acidities as Measures of Carbanion Stabilities. The Relative Effects of Phenylthio, Diphenylphosphino, and Phenyl Groups

Sir:

It has become common practice to use rates of deuterium exchange, or the like, to obtain evidence concerning such important questions as the effects of aromaticity,[2] antiaromaticity,[3] homoaromaticity,[4] heteroatom substitution,[5] and s character,[6] on relative carbanion stabilities. It has been clear for some time, however, that interpretation of the kinetic data is made difficult by the existence of factors such as internal return and ion pairing. If internal return is present, as is often the case, the rate-limiting step is not the rate of carbanion formation but rather the rate of exchange of solvent molecules at the carbanion site.[7] If ion pairing occurs, as is true for most of the solvents used for such studies (Et_2O, THF, CHA, NH_3, *t*-BuOH, MeOH, etc.), relative rates may vary markedly, depending on the nature of the cation, the anion, and the solvent. For example, Shatenshtein and Gvozdeva found the ratio of exchange rates, $k^{\varphi SCH_3}/k^{\varphi CH_3}$, to vary from 10^4 to 40 to 0.2 in changing from KNH_2–NH_3 to $NaCH_2SOCH_3$–DMSO to *t*-BuOK–DMSO.[8,9]

To add to these difficulties there is evidence that the Brønsted α coefficient, which relates kinetic to equilibrium acidities, is not readily predictable and may sometimes be anomalous.[12] The existence of Brønsted α coefficients greater than one and less than zero[12] shows that, even when internal return and ion pairing effects are absent, kinetic acidities may misrepresent carbanion stabilities. A coefficient larger than one means that the kinetic acidity has overestimated carbanion stability, as judged by equilibrium acidities. On the other hand, comparisons of kinetic acidities often leads one to underestimate carbanion stabilities. For example, nitromethane is deprotonated by HO^- in water at a rate only *ca.* 100 times that for acetone,[13] whereas the difference in their equilibrium constants is *ca* 10^{10} in water,[14] and $10^{9.7}$ in DMSO.[1] In addition, when substituents are introduced near the acidic site, polar, steric, and/or conjugative effects may affect kinetic acidities in such a way as to indicate an order of carbanion stability the *inverse* of that actually present. The effect of Me substitution on deprotonation rates in the series CH_3NO_2, $MeCH_2NO_2$, and Me_2CHNO_2 is an example where kinetic acidities predict the wrong order of anion stabilities, as judged by equilibrium acidities (negative Bronsted α).[12] We now present what appears to be a similar example from the effects of α-heteroatom substitution.

The relative rates of exchange of phenyl methyl sulfide, dimethylphenylphosphine, and toluene with potassium amide in liquid ammonia have been reported to be: $C_6H_5SC\mathit{H}_3$ (10^4) > $C_6H_5P(C\mathit{H}_3)_2$ (2) > $C_6H_5C\mathit{H}_3$ (1.0).[5] From these results it would appear that the relative order of effectiveness of groups in stabilizing carbanions is $C_6H_5S \gg C_6H_5P > C_6H_5$. The relative effects of the $(C_6H_5)_2P$, C_6H_5S, and C_6H_5 groups have now been assessed by measuring equilibrium acidities in DMSO with methyl phenyl sulfone as the parent acid. The p*K*'s of $GCH_2SO_2C_6H_5$ with G = H, C_6H_5S, $(C_6H_5)_2P$, and C_6H_5 were found to be 29.0_5, 20.3, 20.2, and 23.4, respectively.[16,17] Assuming that the effect on acidity is primarily one of carbanion stabilization,[1] the effects range from 5.9 to 9.1 powers of ten,[18] corresponding to *ca.* 8.0–12.5 kcal/mol at 25°.

It is noteworthy that the effect of the phenyl group on carbanion stability observed is larger (Δ p*K* = 5.6) than any reported previously in solution,[19] and that the effect of the phenylthio group is even larger.[21] The effect of the diphenylphosphino group appears to be slightly larger than that for the phenylthio group, judging from acidities in the G_2CH_2 series; thus, p*K*'s for G = $(C_6H_5)_2P$, C_6H_5S, C_6H_5 were found to be 29.9, 30.8, and 32.3,[22] respectively. It appears, then, that the C_6H_5P group, instead of being much less effective at carbanion stabilization than the C_6H_5S group, as kinetic acidities suggest, may be slightly more effective. It follows from these results that, although kinetic acidities often give a rough guide to carbanion stabilities, conclusions regarding relative carbanion stabilities derived from kinetic measurements must be regarded as tentative, at best.[23]

Acknowledgment. We are grateful to the National Science Foundation (GP-29539X) for support of this investigation.

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(16) We are grateful to Dr. D. J. Peterson for supplying us with a pure sample of $(C_6H_5)_2PCH_2SO_2C_6H_5$.

(17) Measurements were made in pure DMSO at 25°.[1,11] As a consequence of anchoring our p*K* scale to "absolute" measurements made in the 5–12 p*K* region, the values given in earlier papers in this series[1,11] must be adjusted upward by a little over 2 p*K* units. Details will be given in a full paper now in preparation.

(18) The Δ p*K*'s relative to the hydrogen compound (statistically corrected).

(19) For example, the effect of phenyl in increasing the ion pair acidities of hydrocarbons in cyclohexylamine is generally 2 p*K* units, or less, the largest value (4.4) being observed with fluorene as the parent acid.[20]

(20) A. Streitwieser, Jr., J. R. Murdoch, G. Häfelinger, and C. J. Chang, *J. Amer. Chem. Soc.*, **95**, 4248 (1973).

(21) This is true also for other parent carbon acids. Details will be presented in a full paper now in preparation.

(22) This value should be regarded as tentative since it is above the limit for accurate measurements.

(23) Another example of the misleading information relative to carbanion stabilities sometimes given by kinetic acidities is the observation that $(PhS)_3CH$ and $(PhS)_2CH_2$ exchange at almost the same rate under NH_3 catalysis in liquid NH_3.[8,24] In contrast, we find $(PhS)_3CH$ to be more acidic than $(PhS)_2CH_2$ in DMSO by 8.3 p*K* units.

(24) On the other hand, $(EtS)_3CH$ has been reported to undergo *t*-BuOK catalyzed exchange in *t*-BuOH at a rate 379 times that for $(EtS)_2CH_2$.[25]

(25) S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 427 (1964).

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An Application of Fourier Transform Techniques in the Proton Homo Double Resonance Mode. Internuclear Double Resonance

Sir:

Internuclear double resonance (INDOR)[1] is well accepted as one of the convenient methods to find hidden resonance lines and/or to determine relative signs of spin coupling constants in high resolution nmr studies. In this method, the change in level populations as the result of spin pumping is detected through the monitor line as the intensity variation which occurs when the frequency, ω_2, of the perturbing field H_2 coincides with the frequency of a line that has an energy level in common with the monitor line transition at ω_1.

For simplicity, assume a spin coupled two-spin system AB. The energy level diagram is shown in Figure 1. Quantitatively, the intensity of the monitor line corresponding to the transition B_1, for example, increases when the population at the level q increases through spin pumping by the effect of the swept irradiation frequency ω_2. Spin pumping to the level r reduces the intensity of the monitor line. The rf level at the frequency ω_1 for monitoring is adjusted below saturation in an INDOR experiment.[2]

However, consider the spectrum to be measured after the transition B_1 is irradiated by frequency ω_2. The irradiation must be sufficient to perturb the population in levels q and r but be short in time so as not to cause the rearrangement of the population in p and s. The difference in peak intensity of lines corresponding to transitions A_1 and A_2 as measured by conventional single resonance methods and the peak intensities measured using the procedure outlined above must be analogous to the INDOR spectrum.

This kind of peak intensity is maximized if it is observed in a spectrum measured just after the level populations in r and q are interchanged. This measurement, however, is difficult to make using conventional swept mode nmr equipment because the required time to span the whole spectral range is usually long enough to reach thermal equilibrium.

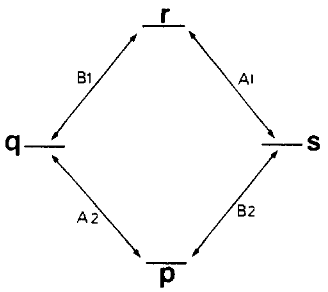

Figure 1. Energy level diagram for AB two spin system. p, q, r, and s show energy levels, respectively, and A_1, A_2, B_1 and B_2 represent allowed transitions, respectively.

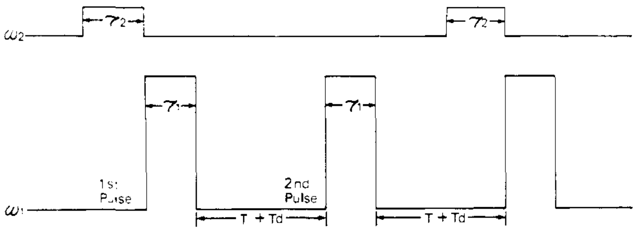

Figure 2. Time sequence of the pulse trains. Pulse at ω_2 is used for irradiation, pulses at ω_1 are observed.

The Fourier transform technique is the best way to solve this difficulty. The information on peak intensity in the frequency domain is available at the beginning of the free induction decay. That is, the information may be correct if data acquisition time is comparable to relaxation time T_1 and if relaxation times of each of lines are not equal.

Figure 2 is a schematic representation of pulse train. To obtain optimum effects at frequency ω_2, the irradiation field strength H_2 and the pulse width τ_2 must meet the relationship $\gamma H_2 \tau_2 = \pi$, where γ is gyromagnetic ratio of a proton, and, in addition, the frequency distribution must be narrow enough so as not to perturb other transitions. In extreme cases, these conditions can be achieved by using continuous wave irradiation; however, this mode of operation causes generalized Overhauser effects[3] or spin tickling,[4] depending on the spin system involved.

The first pulse at frequency ω_1 is used to observe the effect on the irradiation at ω_2. The second pulse at frequency ω_1 is used to measure the spectrum of the spin system at thermal equilibrium in the external magnetic field. The difference in free induction decays after these two kinds of pulses occur is then accumulated and transformed into frequency domain. For a meaningful measurement, the sum of the aquisition time T and the pulse delay time T_d must be long enough compared to all of relaxation times T_1 of the spin system under study.

An experiment to illustrate this principle was carried out on a Varian NV-14 high resolution nmr spectrometer modified for proton FT use. The data system used was a Varian Data Machine's ADAPTS computer system. An internal deuterium lock was used to hold the field/frequency ratio constant. The output frequency of the NV-14's standard spin decoupler was pulsed and amplified to obtain an appropriate pulse for sample irradiation purposes.

The result of one experiment is reproduced in Figure 3. The bottom trace is a part of a normal spectrum of a deuteriochloroform solution of Maltol (Figure 4) measured by using the Fourier transform technique. The middle shows the effect of ω_2 on the same part of the spectrum. The upper one is the result of using the procedure described above. The line at the far left of the trace was irradiated in this ex-