equilibria in the systems $ArCHCH_3NO_2$ and $ArCH_2CHCH_3NO_2$. Although the existence of an inverse relationship, with the necessary corollary that the Brønsted exponent cannot be taken as a guide to the position of the transition state along the reaction coordinate, has been predicted[1] for other carbon acids, none, prior to the present work, has been observed.

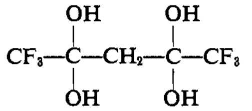
Potentiometric measurements of the acidities of various β-diketones and detritiation studies of the solvent (water) catalyzed rates of ionization (Table I) show that fluorine substitution increases the acidities of the first three compounds much as expected whereas the rates decrease by a factor close to 2 for each trifluoro group substituted. In contrast to these findings substituent effects on both rates and acidities in the benzoyltrifluoroacetones are entirely normal.

Table I. Acidities and Water-Catalyzed Rates of Detritiation of Various β-Diketones at 25°

β-Diketone	pK_a[a]	Lit. value	10^5k^T, sec^{-1}
Acetylacetone	8.99	8.93[5]	66.5
Trifluoroacetylacetone	6.79	6.3[b]	33.3
Hexafluoroacetylacetone	5.3	4.35[6]	15.1
Benzoyltrifluoroacetone	6.54	6.3[b]	38.3
p-Nitrobenzoyltrifluoroacetone	5.38		72.8
p-Methoxybenzoyltrifluoroacetone	6.94		21.6

[a] Uncorrected for either enol or hydrate content. The values refer to C–H ionization, those for the hydrates being considerably higher.[7] [b] J. C. Reid and M. Calvin, *J. Amer. Chem. Soc.*, **72**, 2948 (1950).

This anomalous behavior, resulting as it does from increasing fluorine substitution, can best be seen by comparing the benzoylacetones and benzoyltrifluoroacetones. In the first series the enol content is usually high (~30%)[5] and the extent of hydration small whereas the opposite is true for the fluorine-containing β-diketones. It has previously been observed,[6] for example, that hexafluoroacetylacetone exists in aqueous solution mainly as the dihydrate (1) and ionizes at a very slow rate even in the presence of such a strong base as sodium hydroxide. This is no doubt due to the very small amount of unhydrated ketone present[7] and lends support to the belief that, contrary to some recent work,[8] enolization is still the mechanism for base catalyzed halogenation of aliphatic ketones in aqueous solution.[9]



$$CF_3-C(OH)_2-CH_2-C(OH)_2-CF_3$$

1

The successful operation of the Brønsted equation depends on the fact that as the base or acid is varied the potential energy curves should still have the same shape and same position along the reaction coordinate axis. However in going from benzoylacetone to benzoyltrifluoroacetone the activation energy for the ionization reaction increases by nearly 6 kcal, while the entropy of activation becomes considerably less negative. These differences reflect the importance of hydrogen bonding and hydration in the fluorinated compounds and clearly the necessary conditions for the operation of the relationship no longer prevail.

The effects of fluorine substitution may also lead to an anomalous Brønsted relationship in another series of carbon acids as a number of workers[10] have concluded from deuterium exchange studies that an α-fluorine substituent increases the kinetic acidities of polyhaloaliphatic hydrocarbons whereas for a series of substituted fluoronitromethanes the equilibrium acidities decrease.[11]

Factors other than hydration must be important for these compounds.

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(6) R. W. Taft and E. H. Cook, *J. Amer. Chem. Soc.*, **81**, 46 (1959).

(7) R. Stewart and R. Van der Linden, *Can. J. Chem.*, **38**, 399 (1960).

(8) C. Rappe, *Acta Chem. Scand.*, **20**, 1721 (1966); **22**, 219 (1968).

(9) C. G. Swain and R. P. Dunlap, *J. Amer. Chem. Soc.*, **94**, 7204 (1972).

(10) (a) J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Amer. Chem. Soc.*, **79**, 1406 (1957); (b) S. Andreades, *ibid.*, **86**, 2003 (1964).

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Received August 4, 1973

Application of Kinetics in Highly Basic Media to the Determination of Carbon (and Other) Acidities

Sir:

Although the acidities of carbon acids cover a wide range,[1] $(-3 \langle pK_a \rangle 30)$ two methods, the competitive[2] and acidity function approach,[3] are more widely used than any of the other methods in determining the pK_a's. However, both have serious limitations, and in this communication a new and versatile method, that incorporates several advantages, is introduced.

The method has its origin in the ability of dipolar aprotic solvents such as dimethyl sulfoxide to not only dramatically increase the basicity of aqueous hydroxide solutions but also the rates of many chemical reactions.[4] The procedure entails measuring the rates of detritiation of a "standard" carbon acid in a series of dimethyl sulfoxide–water solutions containing a fixed concentration of base (0.010 *M* in the present work), *i.e.*, over an H_- range. The procedure is then repeated in the presence of a second acid that is appreciably ionized under these conditions. The resulting decrease in hydroxide ion concentration (and hence H_-) is reflected in a decrease in the rate of detritiation of the "standard" carbon acid. Provided that the second-order rate constant for detritiation in a particular solvent system is indeed constant and that no catalysis of the detritiation by the anion formed from the more acidic acid (A_2H) occurs, the new hydroxide ion concentration is given by

$$[OH^-]_2 = [OH^-]_1 \frac{k_2^T}{k_1^T}$$

k_1^T and k_2^T are the pseudo-first-order rate constants for detritiation in the absence and in the presence of the second acid, respectively. Then

$$[A_2^-] = [OH^-]_1 - [OH^-]_2$$

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(1) J. R. Jones, *Quart. Rev., Chem. Soc.*, **25**, 365 (1971).

(2) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *J. Amer. Chem. Soc.*, **89**, 63 (1967).

(3) K. Bowden, *Chem. Rev.*, **66**, 119 (1966).

(4) J. R. Jones, *Chem. Brit.*, **7**, 336 (1971).

and

$$[A_2H] = [A_2H]_{\text{initial}} - [A_2^-]$$

which on substitution in the familiar equation

$$H_- = pK_{A_2H} - \log [A_2^-]/[A_2H]$$

gives the required pK_a.

The second-order rate constants have been found to be independent of hydroxide ion concentration in a number of dimethyl sulfoxide–water solutions of varying composition and the acidity constants show no perceptible trend with increasing concentration of any of the A_2H acids so that the two main requirements necessary for the successful operation of the method are well obeyed. The method also depends on having the solutions carefully degassed and being able to perform the detritiations under an inert atmosphere of nitrogen. The acidities can be quoted to within ±0.1 p*K* unit, and the general validity of the method has been established by redetermining the pK_a of fluorene, which has been the subject of several studies, and also that of 2-nitro-4-chloroaniline, one of the nitrogen indicators used in setting up the H_- scale.[5] The "standard" acid used was [9-^{3}H]-9-*tert*-butylfluorene. The acidities of two acetophenones and two benzylideneacetones are also given in Table I.

Table I. Acidities in the Dimethyl Sulfoxide-Water Solvent System at 25°

Acid	pK_a	Lit. value
Fluorene	21.0	22.94,[2] 22.83,[a] 20.5,[b] 21.0,[c] 22.1[d]
2-Nitro-4-chloroaniline	16.9	17.1,[5] 17.2[e]
p-Cyanoacetophenone	18.4	
p-Dimethylaminoacetophenone	22.6	
Benzylideneacetone	21.4	
p-Cyanobenzylideneacetone	20.6	

[a] A. Streitwieser, Jr., E. Ciuffarin, and J. I. Brauman, *J. Amer. Chem. Soc.*, **89**, 59 (1967). [b] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 1721 (1967). [c] K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965). [d] K. Bowden and A. F. Cockerill, *J. Chem. Soc. B*, 173 (1970). [e] R. Stewart and J. P. O'Donnell, *Can. J. Chem.*, **42**, 1681 (1964).

The method is well suited for those compounds whose absorption spectra do not undergo significant change on ionization. Furthermore by careful choice of the "standard" acid a wide range of acidities can be covered and the work extended to widely different solvent systems.

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(5) D. Dolman and R. Stewart, *Can. J. Chem.*, **45**, 911 (1967).

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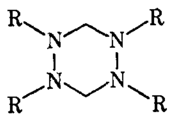
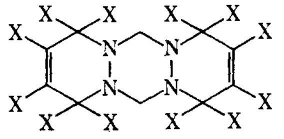
Conformational Equilibria of Hexahydrotetrazines

Sir:

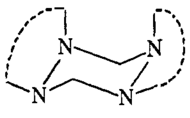
1,2,4,5-Tetramethylhexahydro-1,2,4,5-tetrazine (**1**) can exist as five chair conformers **1-V** to **1-Z** containing up to two axial methyl groups, of which **1-V**, with two axial groups on the same side of the ring, can be neglected. Anderson and Roberts[1] interpreted the low-temperature nmr spectrum in terms of a conformer with two axial methyl groups and postulated that the most likely conformer was **1-X**. Our group supported[2] **1-W** on the basis of dipole moment evidence. Nelsen and Hintz[3] claim to have demonstrated, from nmr comparisons with polycyclic compounds, including **3**, that **1** exists as conformer **1-X**, and ascribe the dipole moment results[2] to impurities. They further claim[3] that the tetraethyl analog (**2**) exists 85% as the conformer **2-W** and 15% as **2-X**. Unfortunately their work contains serious errors of assignment and interpretation as well as an unjustified slight on our experimentation and we now show that their conclusions[3] are both quantitatively and qualitatively incorrect, by using 220-MHz spectra of a selectively deuterated compound.



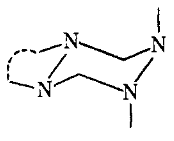
1, R = Me
2, R = Et



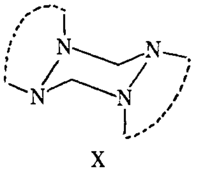
3, X = H
4, X = D



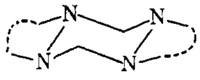
V



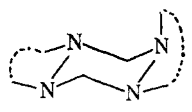
W



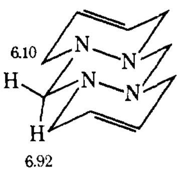
X



Y



Z



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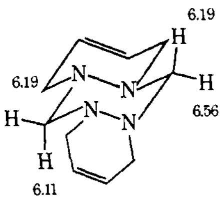

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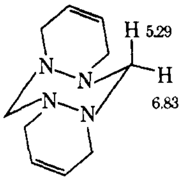

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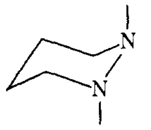

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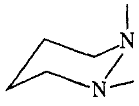

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The tricyclic derivative **3** provides the key to the assignment of the nmr spectra of the monocyclic compounds **1** and **2**. Nelsen and Hintz[3] interpret the low-temperature nmr spectrum of **3** in terms of a single conformer **3-Z**; as will be discussed in the full paper this is easily seen to be incorrect from the spectrum of **3** itself. Further, the low-temperature spectrum (Figure 1) of the selectively deuterated analog **4** clearly demonstrates the presence of the three conformers **3-Z**, **3-X**,

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(1) J. E. Anderson and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 4186 (1968).

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(3) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **94**, 3138 (1972).