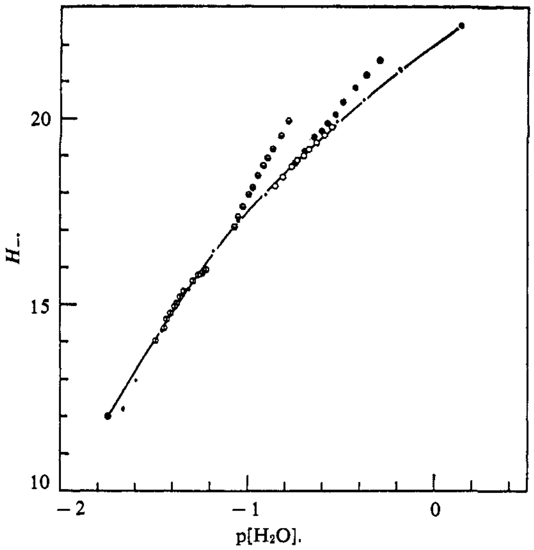
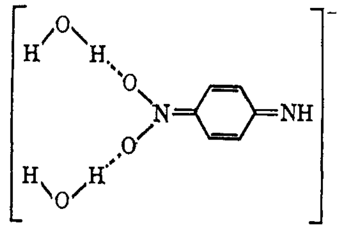


Figure 1. Base strength of aqueous DMSO solutions as a function of water concentration: ⦶, 2,4-dinitrodiphenylamine, [KOH] = 10 m*M;* ○, 4-nitroaniline, [KOH] = 10 m*M;* •, calculated from data in ref 7, $[Me_4N^+OH^-]$ = 11 m*M* adjusted to 10 m*M;* ◒, 9-phenylfluorene (p*K* = 18.1 assumed), [KOH] = 10 m*M;* ●, fluorene (p*K* = 21.1 assumed), [KOH] = 10 m*M*.

The p*K*'s of PFH and FH are set at 18.1 and 21.1 so that H_- values measured with them conform to the aniline scale at the higher water concentrations. Clearly, the two types of indicators do not behave ideally relative to each other since the curves are not parallel. Furthermore, the Δp*K* between, say, NAH and PFH will depend strongly on solvent composition, and therefore a large uncertainty is inevitable when absolute p*K* values are assigned to the less acidic hydrocarbons. This same sort of discrepancy obtains also in methanolic DMSO, although it is not as serious. The discrepancy is negligible in ethanolic DMSO.

The causes of the deviations have not been investigated, but it seems likely that the nitro groups are an important factor. Thus if the anion of 4-nitroaniline is stabilized by hydrogen bonding to water, an increase in water concentration would increase the acidity of NAH relative to that of PFH, as is observed. Salting out of the un-ionized hydrocarbon by water, another possible source of nonideality, should have an effect opposite to that observed. It is interesting to note that H_- data measured in methanolic DMSO with 4-nitrotriphenylmethane and with bis(4-nitrobenzyl) sulfone[8] parallel very closely the data from the nitroanilines.



At the present time it appears to us that the nitroaniline scale is the most firmly anchored in the aqueous reference state. Furthermore, it is fairly consistent in a number of aqueous and alcoholic DMSO solutions as well as in pure DMSO. As such, it can be a useful tool. The nonideality between the anilines and the more acidic hydrocarbons creates large uncertainties in the p*K* values assigned to the hydrocarbons, but since the aniline scale is the only available link between the hydrocarbons and the aqueous reference state there is little choice but to use it temporarily as the base for the hydrocarbons. If the hydrocarbon scale can be satisfactorily related directly to the pH scale, then perhaps a more valid and widely applicable H_- scale can be developed. A more detailed description of the H_- scale in a number of alcoholic DMSO mixtures will be given in a subsequent communication.

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(8) Measured in our laboratory by R. H. Imes in cooperation with Dr. F. G. Bordwell.

Acidity in Nonaqueous Solvents. V. Acidity Scales in Dimethyl Sulfoxide Solution[1,2]

Sir:

Using the potentiometric method recently described,[2] we have determined the "absolute"[3] acidities of several additional carbon acids in dimethyl sulfoxide solution. The new data, presented in Table I, along with some pertinent previously reported data, provide an explanation of major discrepancies between reported relative acidities in dimethyl sulfoxide and cyclohexylamine solution[4] and provide further insight into the nature of the effect of changing solvent on the relative acidities of various acids.

Table I. Comparison of Acidities in Various Solvents

Acid	p*K*(DMSO)[a]	p*K*(H_2O)[b]	p*K*(CHA)[c]
9-Carbomethoxyfluorene	10.3	$12.9^{d,e}$	...
p-Nitrophenol	10.4^{f}	7.1	...
Acetic acid	11.6^{f}	4.8	...
Malononitrile	11.0	$11.1^{g,e}$	...
Benzoylacetone	12.1^{f}	9.6	...
Tris(*p*-nitrophenyl)methane	12.2^{f}	$14.3^{d,e}$	...
Acetylacetone	13.4	9.0	...
2,4-Dinitroaniline	14.8^{f}	14.7^{d}	...
Nitromethane	15.9^{f}	10.2	...
9-Phenylfluorene	16.4	$18.6^{d,e}$	(16.4)
Indene	18.5	18.2^{d}	17.8
9-Methylfluorene	19.7^{f}	...	...
4,5-Methylenephenanthrene	20.0	...	20.5
Fluorene	20.5	20.5^{d}	20.6
Triphenylmethane	∼28	$28.8^{d,h}$	29.4

[a] Standard state in dimethyl sulfoxide solution. Estimated accuracy: ±0.3 p*K* unit (see ref 2). All measurements at 25.0°. [b] Those values not referenced were actually determined in aqueous solution. Others have been determined by acidity function techniques. [c] Values taken from ref 4 and adjusted to p*K* = 16.4 for 9-phenylfluorene. [d] Values determined by acidity function techniques. [e] From ref 5. [f] Values from ref 2. [g] Value determined in aqueous solution and used as the standard for establishment of an H_- scale. See ref 5. [h] Personal communication from Dr. E. C. Steiner.

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(1) This work was supported by Grant No. GM 12832 from the Public Health Service, National Institutes of Health.

(2) For previous papers in this series, see: C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1721 (1967), and earlier references cited there.

(3) The word "absolute" is used in the sense that the equilibrium constants are referred to a standard state in the solvent in which they are measured.

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

A pK value of 11.14 for malononitrile in aqueous solution was determined by Bowden and Stewart.[5] This acid was then used as the "anchor compound" to establish an acidity scale in ethanol–dimethyl sulfoxide mixtures. The scale was applied to the measurement of pK values for a number of carbon acids, among which were 9-carbomethoxyfluorene, tris(p-nitrophenyl)methane, and 9-phenylfluorene. The pK(H_2O) values shown in the table for these compounds are those obtained by Bowden and Stewart.

The present data clearly show the breakdown of the acidity scale. The relative acidity of malononitrile and 9-carbomethoxyfluorene changes by 2.5 pK units on going from ethanol to dimethyl sulfoxide solution. The relative acidities of 9-carbomethoxyfluorene and either tris(p-nitrophenyl)methane or 9-phenylfluorene, however, are nearly the same in both determinations.

In now appears probable that the agreement previously reported[2] between our "absolute" pK's and those determined by Steiner[6] by acidity function techniques is purely fortuitous. Apparently, the reference compound, 4-nitroaniline, used by Steiner for determination of the other acids just happens to be one for which the pK is not strongly affected by the change of solvent. Malononitrile appears to be another such compound, showing the same pK in water and dimethyl sulfoxide.

As we discussed in our previous paper,[2] four distinct effects are expected to influence the change in acidity of an acid on going from water to dimethyl sulfoxide. Two of these effects, the greater basicity of dimethyl sulfoxide than water and the dispersion interaction of highly colored anions with solvent, would act to increase acidity in dimethyl sulfoxide. The other two effects, electrostatic effects and hydrogen bonding of solvent to the conjugate base, would decrease acidity in dimethyl sulfoxide. For the nitroanilines and for malononitrile it appears that these effects just balance. We believe that this cancellation is purely fortuitous and even results from different magnitudes of the individual effects in the two cases. Both hydrogen bonding and the dispersion interactions are expected to be greater for the nitroanilines than for malononitrile.

The increase in acidity of 9-carbomethoxyfluorene over that for malononitrile in going from ethanol to dimethyl sulfoxide is most reasonably attributed to the dispersion interactions of the substituted fluorenyl anion with the polarizable solvent.

Two conclusions pertinent to current investigations in the study of acidities of hydrocarbons can be drawn from our present data. First, and in our opinion most important, *the data clearly show that no single* H_- *acidity function applicable to acids of different structures can be constructed to reach into pure dimethyl sulfoxide.* This conclusion is further strengthened by the results of Steiner's recent study.[7]

Second, if the relative acidities of various hydrocarbons in cyclohexylamine solution, determined by Streitwieser,[4] are adjusted to our value of 16.4 for the pK of 9-phenylfluorene, rather than to the previously used value of 18.5, the discrepancies noted between the scales in dimethyl sulfoxide and cyclohexylamine solutions no longer appear, and, in fact, the agreement, as shown in Table I, is even better than might have been expected for two such different solvents.

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[5] K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965).

[6] E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **87**, 382 (1965).

[7] E. C. Steiner and J. D. Starkey, *ibid.*, **89**, 2751 (1967). We wish to express our appreciation to Dr. Steiner for furnishing us with a preprint of this paper.

A Novel Method for the Synthesis of Isomerically Pure Vinyl Halides from Alkynes *via* the Hydroalumination Reaction[1]

Sir:

The addition of bromine to vinylorganoboranes results in the formation of 1,2-dibromoboranes. These derivatives are converted to vinyl halides when treated with water or aqueous sodium hydroxide.[2] Recently, Matteson and Liedtke[3] have suggested that bromine adds *trans* to unsaturated boronic esters, and they have established that deboronobromination involves a stereospecific *trans* elimination. In concurrence with these results is the observation by Brown[2] that bromination of *trans*-1-hex-1-enyl-bis(3-methyl-2-butyl)borane, derived from hydroboration of 1-hexyne with bis(3-methyl-2-butyl)borane,[4] gives after hydrolysis *cis*-1-bromo-1-hexene.

We have now investigated the halogenation of vinylalanes. These derivatives are readily available by hydroalumination of alkynes with diisobutylaluminum hydride in a hydrocarbon solvent.[5] This involves a *cis* addition of the aluminum–hydrogen bond to the triple bond, yielding *trans*-vinylalanes from 1-alkynes and *cis*-vinylalanes from disubstituted alkynes. Treatment of the *trans*-vinylalane derived from 1-hexyne in tetrahydrofuran with various halogens in a 1:1 ratio at −50° produces essentially pure *trans*-1-halo-1-hexenes. Under similar experimental conditions the *cis*-vinylalane obtained from 3-hexyne reacts with bromine or iodine to give the corresponding *cis*-3-halo-3-hexenes. The experimental results are summarized in Table I.

The fact that halogenation of unsaturated alanes proceeds with retention of configuration supports the contention that vinylalanes undergo electrophilic cleavage (1) preferentially at the vinyl carbon–aluminum bond. Formation of vinyl halides from vinylboranes, however, is the result of an addition–elimination reaction (2). It should be noted that the reaction of chlorine with the vinylalane derived from 1-hexyne gives a 70:30 mixture of *trans*- and *cis*-1-chloro-1-hexene, indicating a competition between addition to the double bond and cleavage at the vinyl carbon–aluminum bond.

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[1] This research was supported by National Science Foundation Grants No. GP3521 and GP 6633.

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[3] D. S. Matteson and J. D. Liedtke, *J. Am. Chem. Soc.*, **87**, 1526 (1965).

[4] H. C. Brown, and G. Zweifel, *ibid.*, **83**, 3834 (1961).

[5] G. Wilke and H. Müller, *Ann.*, **629**, 222 (1960); G. Zweifel and R. B. Steele, to be published.