We are in the process of developing an extended version of the McEwen-type pK scale[14] as applied to DMSO solvent. Subsequent papers will report pK values for a variety of parent carbon acids and will show the effect of substituents on their acidities.

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Equilibrium Acidities of Carbon Acids. III.[1] Carbon Acids in the Methane Series

Sir:

In the previous paper[1b] it was shown that the apparent acidities of carbon acids is often highly dependent on solvent. In solvents such as ether, benzene, and cyclohexylamine (CHA), where ion pairing in the salts is important, the apparent acidities of weak acids are usually much greater than in dilute dimethyl sulfoxide (DMSO) solutions, where the salts are highly dissociated. Measurements under the latter conditions allow accurate comparisons of acidities in a single solvent over a wide pK range (0–30) with a minimum of interference from counterion effects. In subsequent papers we will present pK data showing the effects of substituents on the acidities of a variety of carbon acids. In this paper we give pK data on the acidities of a number of parent acids in the methane series, CH_3-EWG, where EWG is one of the electron-withdrawing groups: NO_2, COC_6H_5, $COCH_3$, $SO_2C_6H_5$, SO_2CH_3, or $C{\equiv}N$ (Table I). This is the first direct comparison of the pK's of these fundamental types of weak organic

Table I. Equilibrium Acidities of Carbon Acids of the Methane Series, CH_3EWG, in Dimethyl Sulfoxide (DMSO)

Carbon acid	pK[a]	Indicator	Indicator pK[a]
Nitromethane	15.1[b,c]	FH-9-Ph[d]	15.8[d]
Acetophenone	22.5[c]	TPH[e]	23.3
Acetone	24.25[c]	XH-9-Ph[f]	25.6
Methyl phenyl sulfone	26.75[c,g]	DDH[h]	27.1
Dimethyl sulfone	28.8[c,i]	TH[j]	28.3
Acetonitrile	29.1	TH[j]	28.3

[a] Relative to fluorene (FH) at pK 20.5 as a reference standard; values are not statistically corrected. [b] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 1721 (1967), report 15.9 (determined potentiometrically). [c] This measurement agreed within ±0.1 pK unit with that obtained against a second indicator. [d] 9-Phenylfluorene: C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 2752 (1967), report pK 16.4 (determined potentiometrically). [e] 1,1,3-Triphenylpropene (the abbreviation TP₂H has also been used). [f] 9-Phenylxanthene. [g] Previously reported as 27.[1a] [h] Diphenylyldiphenylmethane. [i] Previously reported as 28.[1a] [j] Triphenylmethane: E. C. Steiner (private communication), obtained ΔpK for TH vs. DDH of 1.2, which corresponds exactly with our value. Steiner's values relative to FH were, however, 0.2 pK unit higher than ours.

(1) For previous papers in this series see: (a) F. G. Bordwell, R. H. Imes, and E. C. Steiner, *J. Amer. Chem. Soc.*, **89**, 3905 (1967); (b) F. G. Bordwell and W. S. Matthews, *ibid.*, **96**, 1214 (1974).

acids. The measurements allow a new comparison of the effects of NO_2, COC_6H_5, etc., groups and provide a basis for future studies of substituent effects.

Previously we reported values for the indicators TPH, XH-9-Ph, and DDH relative to FH as a standard, obtained by overlap experiments using carbon acids in the 20–27 pK range.[1b] We now add the indicators triphenylmethane (TH; pK 28.3) and 9-phenylfluorene (FH-9-Ph; pK 15.8) to this list. It is noteworthy that we find FH-9-Ph to be *ca.* 5 pK units more acidic than fluorene (FH) in DMSO,[2] whereas the difference as determined by H_- techniques is only *ca.* 2.4 pK units in DMSO–EtOH (0–95%) and *ca.* 3.5 units in DMSO–HOH (40–90%).[3] These results emphasize the point that relative acidities of carbon acids will often differ depending on solvent.[1b] In the present instance, however, the differences are not due to ion pairing effects. The salts are presumably highly dissociated in all of these solutions, and the differences arise from the differences in solvating ability of pure DMSO *vs.* DMSO diluted with a protic solvent.[5]

The range of acidities from CH_3NO_2 to CH_3CN is 14 pK units (Table I) corresponding to about 19 kcal/mol in $\Delta G°$. Since preliminary indications are that ΔpK's in DMSO can be correlated with carbanion stabilization energies in DMSO,[6] these differences in acidity are probably due primarily to differences in carbanion stabilization by EWG. In Table II ΔpK's for the CH_3-

Table II. Effects of Electron-Withdrawing Groups on Equilibrium Acidities in Dimethyl Sulfoxide

EWG	ΔpK	
	p-HOC₆H₄EWG[a,b]	CH₃EWG
H	0.0 (16)[c]	0.0 (50)[c,d]
CN	4.8[e]	21
CH₃SO₂	5.6[e]	21
CH₃CO	6.0[e]	26
NO₂	6.6[e,f]	35

[a] E. M. Arnett, T. C. Moriarity, L. E. Small, J. P. Rudolph, and R. P. Quirk, *J. Amer. Chem. Soc.*, **95**, 1492 (1973). [b] Comparable ΔpK's are expected for the series p-CH₃SO₂CH₂C₆H₄EWG (pK = 23.15 for EWG = H) on the basis of a similar ρ of 5.0 (R. H. Imes and W. S. Matthews, unpublished results). [c] pK of parent acid (EWG = H). [d] Estimated pK; see ref 9; the size of ΔpK is dependent on this estimate, but the relative ΔpK's are not. [e] Calculated from σ_R^- values (ref 13) with ρ = 5.3 (see Arnett, *et al.*, footnote a). [f] I. M. Kolthoff, M. K. Chantooni, and S. Bhownik, *J. Amer. Chem. Soc.*, **90**, 23 (1968), found ΔpK to be 5.4 (pK p-NO₂C₆H₄OH = 11.0); a ΔpK of 6.0 is obtained by using the pK of 10.4 for p-NO₂C₆H₄OH reported by C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 2752 (1967).

(2) This is the statistically corrected difference. The value for FH-9-Ph may be subject to minor uncertainty (perhaps ±0.2 pK) since it has been linked to FH through 4-nitroaniline, which we no longer consider to be completely reliable as an indicator.

(3) K. Bowden and A. F. Cockerill, *J. Chem. Soc. B*, 173 (1970). These ΔpK values do not appear to have been statistically corrected (add 0.3 to ΔpK for statistical correction). The pK in sulfolane–H₂O is 0.1 pK unit higher than that in DMSO–H₂O.[4]

(4) R. L. Burwell, Jr., and C. H. Langford, *J. Amer. Chem. Soc.*, **82**, 1503 (1960).

(5) See C. D. Ritchie, "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 4, for a discussion of solvent effects in DMSO.

(6) Judging from the reasonable agreement found by Ritchie and Uschold for the pK's of p-nitro- and tris-p-nitrotriphenylmethanes with those calculated from carbanion stabilization energies,[7] as determined by McKeever and Taft.[8]

(7) C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 1721 (1967).

(8) L. D. McKeever and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 4544 (1966).

EWG acids, based on a pK of 50 for methane,[9] are compared with those of phenols.

Examination of Table II shows that, as would be expected, the acidifying effects of EWG are greatly exaggerated when it is attached directly at the acidic site (CH$_3$EWG) instead of across a benzene ring. Note, for example, that a p-NO$_2$ group enhances the acidity of phenol in DMSO by ca. 6 pK units, whereas the effect on methane is 35 or more pK units, depending on the pK assigned to methane.[9,12] The relative order of effects remains essentially the same, however, i.e., NO$_2$ > CH$_3$CO > CH$_3$SO$_2$, CN, which is the order expected if the stronger delocalizing effect of CH$_3$CO, relative to CH$_3$SO$_2$ or CN, overrides its much weaker inductive effect (σ_R- for CH$_3$CO is 0.47 compared to 0.38 and 0.33 for CH$_3$SO$_2$ and CN; the corresponding σ_I values are 0.28, 0.59, and 0.56[13]).

The magnitude of the ΔpK values for the methane series is impressive. The estimated minimum increase in acidity of 35 pK units on substitution of a nitro group for a hydrogen atom of methane corresponds to 48 kcal/mol of stabilization energy in the resulting anion.

(9) Estimates of the pK of methane range from 40 to 84.[10] A linear extrapolation from CH$_2$(CN)$_2$ (pK 11.0 in DMSO[4]) to CH$_3$CN (pK 29.1 in DMSO (Table I)) to CH$_4$ gives a pK of 47 for methane. It seems likely, however, that ΔpK for the change from CH$_3$CN to CH$_4$ is much larger than that from CH$_2$(CN)$_2$ to CH$_3$CN. The value of 47 also appears to be too low based on an estimated pK of benzene as ca. 49 in DMSO. The latter estimate is based on Streitwieser's extrapolated value of 43 for benzene in CHA.[11] Since we find that the pK of phenyl-acetylene,[1b] a carbon acid forming a localized carbanion similar to that obtained from benzene, is ca. 6 units higher in DMSO than in CHA, an increment at least as large can be assumed for benzene. A pK of 50 for methane in DMSO appears minimal from these considerations, and a considerably higher value, say 60, does not appear unreasonable.

(10) See (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter I; (b) A. Streitwieser, Jr., W. C. Langworthy, and J. J. Brauman, J. Amer. Chem. Soc., 85, 1761 (1963).

(11) A. Streitwieser, Jr., P. J. Scannon, and H. H. Neimeyer, J. Amer. Chem. Soc., 94, 7936 (1972).

(12) A single p-NO$_2$ group increases the acidity of triphenylmethane in DMSO by ca. 12 pK units.[7]

(13) S. K. Dayal, S. Ehrenson, and R. W. Taft, J. Amer. Chem. Soc., 94, 9113 (1972).

(14) National Science Science Foundation Postdoctoral Fellow, 1971–1972.

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Transition Metal Promoted Redirection of the Thermal Bishomoconjugative Bond Reorganization Pathway of Unsaturated Propellanes

Sir:

Thermolysis of tricyclic [4.2.0]octatrienes of general formula 1 above 400° in the gas phase (contact times of 1–3 sec) is recognized not to involve aromatization with loss of acetylene (symmetry disallowed) but rather to proceed with formation of the structurally isomeric cyclooctatetraenes, 3, in good yields.[1] Appropriate

(1) L. A. Paquette and R. E. Wingard, Jr., J. Amer. Chem. Soc., 94, 4398 (1972).

deuterium labeling studies and other experiments have implicated an intramolecular $(4 + 2)\pi$ cycloaddition pathway for these rearrangements and subsequent valence isomerization (if suprafacial, symmetry allowed) of the cis^2-bishomobenzene intermediates, 2.

$\underset{\sim}{1}$ $\qquad$ $\underset{\sim}{2}$ $\qquad$ $\underset{\sim}{3}$

$\underset{\sim}{a}$, n = 2 ; $\underset{\sim}{b}$, n = 3
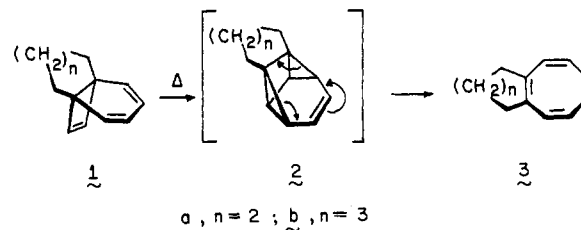
The marked preference for the Diels–Alder bishomo-conjugative mechanism in such systems is further reflected specifically in the thermal self-interconversions of cyclooctatetraenes[2] and, less categorically, in the behavior of a wide array of [4.2.2] and [4.2.1] bicyclic structures.[3] We have considered the possibility that this interesting pathway, requiring as it does the involvement of all six pπ electrons in 1, could be blockaded and perhaps redirected in the presence of a transition metal. Such an alternate bond reorganization pathway has been observed and forms the subject of this report.

When 1a was heated at reflux with 30 mol % Mo(CO)$_6$ (freshly sublimed) in anhydrous benzene under a purified nitrogen atmosphere for 36 hr, isomerization to 3a (41% isolated[4]) was observed. Control experiments involving the heating of 1a in refluxing benzene for >2 days resulted in total recovery of unchanged propellane. In contrast, reaction of 1a with the more reactive Mo(CO)$_3$(diglyme)$_3$ reagent[5] in diglyme–benzene (10:3) at 25° for 18 hr led to formation of complex 4a (43%), obtained as pale yellow crystals, mp 90–92° (from pentane). The nmr spectrum of 4a [δ(CDCl$_3$) 5.57 (s, 2 H), 4.69 (s, 2 H), 4.60 (s, 2 H), 2.4–2.0 (m, 4 H), and 1.1–1.75 (m, 4 H)] suggested complexation of molybdenum to 1,5-olefinic groups in the bicyclic valence isomer as expected of the specific geometrical requirements of the coordinated Mo(CO)$_4$ moiety.[6] This conclusion was confirmed and the complete stereochemistry of the complex revealed by three-dimensional X-ray crystal structure analysis (Figure 1).

Systematic extinctions uniquely required the space group $P2_1/n$ (C^5_{2h}-alternate setting) with four molecules in a unit cell of dimensions $a = 17.962$ (5), $b = 11.944$ (3), $c = 7.125$ (2) Å, and $\beta = 93.65$ (2)°. All crystals that were examined were polysynthetic twins in which

(2) (a) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., J. Amer. Chem. Soc., 94, 9224 (1972); (b) L. A. Paquette and M. Oku, ibid., 96, 1219 (1974).

(3) (a) W. von Philipsborn, J. Altman, E. Babad, J. J. Bloomfield, D. Ginsburg, and M. B. Rubin, Helv. Chim. Acta, 53, 725 (1970); (b) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., J. Amer. Chem. Soc., 95, 2230 (1973); (c) M. J. Goldstein and S. A. Kline, Tetrahedron Lett., 1089 (1973), and references contained in these papers.

(4) This rearrangement was accompanied by the formation of significant amounts of dark intractable material.

(5) T. H. Coffield and R. P. M. Werner, U. S. Patent 3,124,600; Chem. Abstr., 60, 15914 (1964); R. P. M. Werner and T. H. Coffield, Chem. Ind. (London), 936 (1960).

(6) For earlier examples see (a) E. O. Fischer and W. Frölich, Chem. Ber., 92, 2995 (1959); (b) M. A. Bennett and G. Wilkinson, Chem. Ind. (London), 1516 (1959); (c) H. D. Kaesz, S. Winstein, and C. G. Kreiter, J. Amer. Chem. Soc., 88, 1319 (1966); Y. Menachem and A. Eisenstadt, J. Organometal. Chem., 33, C29 (1971).