The Equilibrium Acidity of Phenylacetylene

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Equilibrium acidities based on an absolute scale are reported for 2,4-dinitro-, 2,6-dichloro-4-nitro-, 4-nitro-, 2,6-dichloro-, and 2,4-dichloro-aniline indicators in dimethyl sulphoxide (Me_2SO) solution (p*K* values: 15.85, 17.4, 20.9, 24.8, and 26.2, respectively). Redetermination of the acidity of phenylacetylene in Me_2SO against a new indicator, 9-(*p*-methoxyphenyl)xanthen (p*K* = 28.4) gave p*K* = 28.7, which agrees well with a previous value (28.8) obtained using two other indicators. This value was not affected appreciably by changing the counterion from K^+ to Na^+, by the presence of 18-crown-6, or by adding small amounts of water. The calculated p*K* of $PhC{\equiv}CH$ of 21 in water is discussed in light of the higher value in Me_2SO.

RECENTLY our published p*K* of 28.8 for phenylacetylene in dimethyl sulphoxide (Me_2SO) solution was rejected in favour of a value of 6.2 p*K* units lower.[1] The lower value was based on ' the pH values at half-neutralization by dimsyl anion ($CH_3SOCH_2^-$) in Me_2SO solution measured with the appropriate (aniline) indicator '. The authors reported their p*K* values to be accurate to ± 0.07 p*K* unit in the 14—24 p*K* range studied. We had previously reported our p*K* values, measured by a similar method, to be accurate to ± 0.01 p*K* unit in this region (and in the 24—32 p*K* region).[2] How is it possible for similar measurements on the same compound, both seemingly accurate to at least two significant figures, to differ by over 10^6? From our studies and from reports from other laboratories we were aware of at least five possible factors that could contribute to the discrepancy in results: (*a*) the choice of an anchor for the acidity scale, (*b*) differences in the nature of the cation used, (*c*) the presence of small amounts of water in the Me_2SO solvent, (*d*) failure to use internal standardization of the base, and (*e*) contact of the highly basic solutions used with oxygen during the runs. We now report experiments carried out to determine what role, if any, each of these factors might play.

Anchoring Acidities on an Absolute Scale.—Our scale was originally anchored[2] on the p*K* values of three carbon acids, 9-cyano- and 9-methoxycarbonyl-fluorenes and malononitrile, determined potentiometrically by Ritchie and Uschold in the p*K* region 8 to 11.[3] Since then the scale has been anchored further by direct spectrophotometric measurements on other compounds in the 2 to 10 p*K* region.[4] Above a p*K* of 14 the potentiometric method has been found to be unreliable, apparently due to slow electrode response.[5] Anchoring of the scale on p*K* = 14.8 for 2,4-dinitroaniline,[1] determined potentiometrically,[3] is one source of discrepancy for the results mentioned above.[1,2]

The accuracy of the overlapping indicator method depends on using numerous cross checks with indicators and standard acids. In order to cover the p*K* range 2—32 we have used over 30 indicators and over 30 standard acids.[2,4] The method is illustrated in Table 1 which gives values for five aniline indicators in the p*K* range 15.8—26.2. The values for 4-nitro-, 2,6-dichloro-, and 2,4-dichloro-anilines differ from those reported,[1] even after a correction for the difference in anchor point has been made.

Examination of Table 1 shows that as much as 3.2 p*K* units of the discrepancy in the results from the two laboratories[1,2] arises from differences in p*K* values assigned to the aniline indicators.

TABLE 1

Establishment of the acidities of a number of aniline indicators in dimethyl sulphoxide solution

Aniline	p*K*[a]	p*K* (lit.)	Standard acids (p*K* values)[e]
2,4-Dinitro-	15.85	14.8[b]	2-Nitropropane (16.78) Nitrocyclohexane (16.21) Nitrocycloheptane (15.78) 9-Phenylthiofluorene (15.40)[f] 9-(*m*-Chlorophenyl)-fluorene (16.83)[f]
2,5-Dichloro-4-nitro-	17.37	16.16	Diphenylacetonitrile (17.5)
4-Nitro-	20.93	19.24[c]	*m*-Fluorophenyl-acetonitrile (19.95)
		18.4[d]	*m*-Chlorobenzyl sulphone (21.44) *m*-Trifluoromethylbenzyl sulphone (20.90)
2,6-Dichloro-	24.80	22.55[c]	1,3,3-Triphenylpropene (25.6)[f] t-Butylfluorene (24.35)[f]
2,4-Dichloro-	26.24	23.44[c]	1,3,3-Triphenylpropene (25.6)[f] 9-(*m*-Chlorophenyl)-xanthen (26.6)[f]

[a] Average of runs with several standard acids (or indicators). [b] Reference 3. [c] Reference 1. [d] E. C. Steiner and J. D. Starkey, *J. Amer. Chem. Soc.*, 1967, **89**, 2751 selected this p*K*, determined by the H_- method and therefore based on the ' aqueous reference state,' to anchor their scale. [e] The p*K* values of these standard acids (or indicators) were determined by multiple runs with more than two indicators (or standard acids). [f] Used as an indicator at a wavelength where the visible absorption did not interfere with that of the aniline.

Ion Pairing Effects.—A second possible source of the discrepancy in results is the use of Na^+ counterion in one laboratory[1] and K^+ counterion in the other.[2] The conductance data of Exner and Steiner show that the ion-pair tendency of cations in Me_2SO solution increase in the order $K^+ < Na^+ < Li^+$.[6] They found that $CH_3SOCH_2^-Cs^+$ and $CH_3SOCH_2^-K^+$ behaved as strong 1 : 1 electrolytes in 0.01M-Me_2SO solution, but that $CH_3SOCH_2^-Na^+$ and $CH_3SOCH_2^-Li^+$ exist partly as ion pairs. Earlier, we have presented this and other reasons for believing that pK determinations carried out in dilute Me_2SO solution with $CH_3SOCH_2^-K^+$ as the base (our base concentrations are usually in the 1—5mM range) are usually free of ion pairing effects.[2] The negative charge in the $PhC{\equiv}C^-$ anion is localized, however, and ion pairing with cations could be much stronger than with $CH_3SOCH_2^-$ or delocalized hydrocarbon anions. There is, in fact, evidence for the formation of relatively stable ion pairs of the type $PhC{\equiv}C^-M^+$ in solvents of low dielectric constant from comparisons of acidities in various media.[2] It seemed possible, therefore, that some ion pairing between $PhC{\equiv}C^-$ and K^+ might occur in Me_2SO. Ion pairing between $PhC{\equiv}C^-$ and Na^+ would then be expected to be greater, and this could contribute to the pK difference obtained for measurements where the cation was Na^+,[1] as compared to measurements where the cation was K^+.[2] A test for ion pairing with $PhC{\equiv}C^-K^+$ was made by inclusion of an equivalent of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) in the solutions used for the pK measurements (Table 2). The effect of the Na^+ cation was tested by carrying out pK measurements using a solution of $CH_3SOCH_2^-Na^+$ in Me_2SO prepared by the reaction of $NaNH_2$ with dry Me_2SO under argon (Table 2).

TABLE 2

Equilibrium acidities of phenylacetylene in dimethyl sulphoxide solution

Indicator (I)	pK_I	p$K_{obs.}$
DDH[a]	(29.4)	28.77
DDH		28.64 ± 0.05[e]
DDH		28.43 ± 0.18[e]
PXH[b]	(27.9)	28.80 ± 0.02
PXH		26.68 ± 0.03[e]
PXH		28.58 ± 0.01[e]
PMPXH[c]	(28.43)[d]	28.64 ± 0.01
PMPXH		28.70 ± 0.015
PMPXH		28.49 ± 0.06[f]
PMPXH		28.48 ± 0.01[f]

[a] *p*-Diphenylyldiphenylmethane. [b] 9-Phenylxanthen. [c] 9-*p*-Methoxyphenylxanthen. [d] The pK of this indicator has been established by J. C. Branca by overlap with the standard acids $PhSO_2CH_3$ (pK = 29.0) and *m*-$BrC_6H_4NH_2$ (pK = 28.4) and the standard indicators DDH and 9-*m*-chlorophenylxanthene (pK = 26.6). [e] Experiments carried out in the presence of *ca.* one equivalent of 18-crown-6 ether (see footnote *). [f] Experiment carried out using $MeSOCH_2^-Na^+$ as the base instead of $MeSOCH_2^-K^+$.

The original assignment of pK 28.8 for $PhC{\equiv}CH$ was based on titrations with two indicators, *p*-biphenylyldiphenylmethane (DDH) and 9-phenylxanthen (PXH).[2] The data for these runs are given in Table 2 as the first entry opposite these indicators. As a check on this assignment we made a measurement against a third indicator, 9-*p*-methoxyphenylxanthen (PMPXH), which has a pK closer to that of $PhC{\equiv}CH$ than does either DDH or PXH, and should therefore give more accurate results. The pK observed, 28.7, is probably a better value than that previously reported (28.8). Runs using DDH and PXH as indicators in the presence of 18-crown-6 gave an average pK of 28.6, which is within the experimental error of our measurements in this pK region.* When $CH_3SOCH_2^-Na^+$ in Me_2SO was used (PMPXH indicator) the pK values observed were *ca.* 0.2 unit lower. These results indicate that ion pairing with $PhC{\equiv}C^-K^+$ and $PhC{\equiv}C^-Na^+$ is not appreciable and rules this out as a factor that might account for the remaining 3.0 pK unit discrepancy.†

The results of these experiments leave little doubt that the pK of $PhC{\equiv}CH$ in Me_2SO is 28.7 ± 0.1 [2] rather than 22.6.[1] (It should be noted in this regard that, according to our results, the least acidic aniline indicator listed in Table 1 is over 2 pK units more acidic than $PhC{\equiv}CH$, and is therefore not suitable as an indicator for measuring an accurate pK for $PhC{\equiv}CH$, contrary to the previous report.[1]) This conclusion is supported further by Arnett's measurements of the heats of deprotonation of $PhC{\equiv}CH$ with $CH_3SOCH_2^-K^+$ in Me_2SO. The ΔH_D obtained for $PhC{\equiv}CH$ fits on the line drawn for the plot of ΔH_D *vs.* pK (our values) for over 40 weak acids covering the pK range 8—30.[7] The conclusion is also supported by the fact that good agreement is obtained between our pK values and those obtained independently by Shatenshtein and his co-workers in Me_2SO using an indicator method anchored on an arbitrary standard.[8] Conversion of Shatenshtein's values into our absolute scale shows agreement to within ± 0.3 pK units for 15 compounds in the pK range 11—32, including DDH, one of the indicators used to measure the pK of phenylacetylene (Table 2).

The Effect of Water on the Acidity of Phenylacetylene.—An upper limit for the pK of $PhC{\equiv}CH$ in water of 21 has been calculated from the rates of amine-catalysed exchange of tritium in $PhC{\equiv}CT$.[9] Although the calculated pK value of 21 in water, which happens to correspond to the ion pair pK of 21 in benzene on McEwen's scale (arbitrary standard),[9,‡] has been referred to as 'the generally accepted value',[11] the large difference between this value and that in Me_2SO (7.7 pK units)

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* In three of these experiments the 18-crown-6 (>99% pure by v.p.c.) was present in the solution during the titration of the indicator with base to determine the extinction coefficient.[2] The base concentrations calculated from these runs was, however, only about one-half that determined in other titrations, indicating the presence of an acidic impurity in the 18-crown-6. This was confirmed by titration of DDH with the 18-crown-6 solution. An 18-crown-6 sample was then purified by removal of water by azeotropic distillation with benzene, followed by short-path distillation at 125° under vacuum (2 mm). A solution of this sample did not cause a decrease in absorbance of the anion from DDH. Repetition of the titration of $PhC{\equiv}CH$ using this sample and DDH as the indicator gave pK = 28.64 ± 0.05. The good agreement between this and the other three runs (Table 2) shows that the impurity was too acidic to interfere with the equilibrium between the indicators and $PhC{\equiv}CH$.

† W. N. Olmstead (unpublished data) has found that $PhC{\equiv}C^-$ in Me_2SO fails to respond to an ion pairing test with K^+ that he has devised.

‡ McEwen's value rests on an ***arbitrary*** anchor point (the pK of MeOH in MeOH).[10] This together with the ion-pairing effects in benzene (or ether) makes comparison of McEwen's 'pK values' with those in water meaningless. The data of Kresge and Lin therefore provide the first and only evidence for the pK of $PhC{\equiv}CH$ in water. In a personal communication Professor Kresge has indicated that his estimate conceivably could be low by as much as 2 or 3 pK units. Nevertheless, phenylacetylene appears to be a stronger acid in water than in Me_2SO by at least 5 pK units.

makes it somewhat suspect. This difference in pK values in H_2O and Me_2SO solvents (ΔpK) is almost as large as *that for* phenols or nitroalkanes, where the negative charge is largely localized on oxygen.[2] The latter large ΔpK is believed to be caused primarily by strong hydrogen bonding of the anion at oxygen in water and the absence of hydrogen bonding of the anion in Me_2SO.[2,5] If this explanation is correct, hydrogen-bonding of these oxygen anions and of the $PhC{\equiv}C^-$ ion in water must be of the order of 10 kcal mol^{-1}, since it is known that for an equilibrium of the type shown in equation (1) (S = solvent) the greater basicity of Me_2SO *vs.* H_2O will tend to *increase* the acidity in Me_2SO by *ca.* 4.5 kcal mol^{-1}.[12]

$$PhC{\equiv}CH + S \rightleftharpoons PhC{\equiv}C^{-}\cdots S + S\text{-}H^{+} \quad (1)$$

To our knowledge there is no experimental evidence for H-bonding to negatively charged carbon. Hydrocarbons giving carbanions in which the negative charge is delocalized, such as fluorene, appear to be more acidic in Me_2SO than in H_2O, indicating the presence of little or no H-bonding.[2] It is possible, of course, that when the negative charge is localized on carbon, as in the $PhC{\equiv}C^-$ ion, strong H-bonding may occur, and that the pK of $PhC{\equiv}CH$ in water may indeed be appreciably lower than in Me_2SO.[9] This could mean that the $PhC{\equiv}C^-$ ion in Me_2SO solution would compete favourably with the solvent as an H-bond acceptor for small amounts of water causing an apparent increase in acidity. It was, therefore, of interest to test this possibility by determining the effect of the presence of small amounts of water in a pK determination for $PhC{\equiv}CH$ in Me_2SO.

Addition of 5 equivalents of water (0.07 mol %), relative to the concentration of $CH_3SOCH_2^-K^+$, to the absorption cell in this determination was found *not* to affect the pK of $PhC{\equiv}CH$ (pK observed $= 28.7 \pm 0.03$, relative to 9-*p*-methoxyphenylxanthen indicator). This shows that a small amount of water *per se* does not cause an apparent increase in the acidity of $PhC{\equiv}CH$. However, the apparent concentration of the stock base, as calculated from an internal titration,[2] was found to be significantly smaller in this determination (67mM) than the value recorded in analogous runs where H_2O had not been added (88mM). It would appear that the $CH_3SOCH_2^-$ anion is reacting with water to establish an equilibrium with (the less basic) HO^- ion, which bonds more strongly with H_2O than does the $PhC{\equiv}C^-$ ion or the Me_2SO solvent. Addition of 12 equivalents of water to a cell containing stock $CH_3SOCH_2^-Na^+$ in Me_2SO (135mM) lowered the apparent base concentration to 41mM. This much lower apparent base concentration is probably caused by further hydration of HO^- ion and possibly ion pairing with Na^+. Studies of Arshadi and Kebarle have shown that the successive addition of 1, 2, 3, 4, and 5 water molecules to HO^- ion in the gas phase release 16.9, 10.7, 7.7, 5.4, and 4.2 kcal mol^{-1} of energy (ΔG°) respectively.[13]

These experiments emphasize the importance of using internal titrations to establish the concentration of the base,[2] particularly in high pK regions. An external titration gives merely the total base concentration (strong and weak). The internal titration measures the concentration of base that is strong enough to deprotonate the indicator under the titration conditions. Exposure of the strongly basic stock solutions to the atmosphere results in the absorption of water and oxygen, which weakens the base. This contamination will not affect the titration, however, unless the base becomes too weak to be effective against the indicator to be used in the titration. It is possible that the difference in the method used to establish the concentration of the stock base in the two laboratories[1,2] may be an additional factor causing the discrepancy in the results. Finally, we have observed that highly basic indicator anions often react rapidly with oxygen. This source of error may be minimized by avoiding low concentrations of indicator. (This may necessitate working on the shoulder rather than at $\lambda_{max.}$.)

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REFERENCES

[1] J. Chrisment and J.-J. Delpuech, *J.C.S. Perkin II*, 1977, 407.

[2] W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *J. Amer. Chem. Soc.*, 1975, **97**, 7006.

[3] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, 1976, **87**, 1721.

[4] J. C. Branca, unpublished data.

[5] C. D. Ritchie, 'Solute-Solvent Interactions,' J. F. Coetzee and C. D. Ritchie, ed., Marcel Dekker, New York, vol. 2, 1976, ch. 4.

[6] H. H. Exner and E. C. Steiner, *J. Amer. Chem. Soc.*, 1974, **96**, 1782.

[7] E. M. Arnett, D. E. Johnston, L. E. Small, and D. Oancea, *Faraday Symposium* No. 10, 1975.

[8] M. I. Terekhova, E. S. Petrov, S. P. Mesyats, and A. I. Shatenshtein, *Zhur. obshchei. Khim.*, 1975, **45**, 1529 (English translation).

[9] A. J. Kresge and A. C. Lin, *J.C.S. Chem. Comm.*, 1973, 761; A. J. Kresge, *Accounts Chem. Res.*, 1975, **8**, 354.

[10] W. H. McEwen, *J. Amer. Chem. Soc.*, 1936, **58**, 1124.

[11] J. E. Crooks, 'Proton-Transfer Reactions,' eds., E. F. Caldin and V. Gold, Chapman and Hall, London, 1975, ch. 6, p. 165.

[12] I. M. Kolthoff and M. K. Chantooni, *J. Phys. Chem.*, 1972, **76**, 2024.

[13] M. Arshadi and P. Kebarle, *J. Phys. Chem.*, 1970, **64**, 1483.