Thermodynamic and Kinetic Acidities in Dimethyl Sulphoxide. Part 2.[1] Acetylenic Compounds

By **Jacques Chrisment** and **Jean-J. Delpuech,*** Laboratoire de Chimie Physique Organique, Equipe de Recherche Associée au CNRS, Université de Nancy I, C.O. 140, 54037 Nancy Cedex, France

The p*K* values and proton transfer rates in anhydrous dimethyl sulphoxide are reported for three monosubstituted acetylenes (1)—(3) RC≡CH (R = Ph, $MeOCH_2$, or Me_2NCH_2). The p*K* values were measured using a set of overlapping indicators: p*K* = 22.6, 23.5, and 24.2 for (1)—(3) respectively. Proton transfers were carried out by conjugate acetylide ions, arising from small additions of methylsulphinylmethanide (dimsyl) anion. Rate constants k_1 followed the order of decreasing acidities: k_1 2.92×10^6, 3.93×10^4, 2.92×10^3 l mol^{-1} s^{-1} at 25 °C for (1)—(3) respectively. The contribution from the dimsyl anion, though negligible, was also taken into account.

THE ionization of carbon acids has been the object of much interest during the last few years.[2-5] In addition to the significant peculiarites of the proton chemistry,[6] a further point of interest is the importance of carbanions in organic synthesis.[7] Their mean lifetime, and therefore their reactivity, may determine the nature and yield of products. The kinetics of their formation and disappearance is therefore relevant in this connection. Ionization rates have been determined for a variety of systems, mainly hydrocarbons such as fluorenes and arylmethanes, nitroalkanes, and carbon acids in which the developing carbanion is activated by a nitro, carbonyl, cyano, or sulphonyl group. Some acetylenic hydrocarbons have been studied in water and in water–t-butyl alcohol or water–pyridine mixtures.[8-12] In all cases, hydroxide ion was the attacking base. The rates thus obtained may not reflect the reactivity of unsolvated species, on account of the strong solvation of anions in these solvents, especially of hydroxide base, and also presumably of the transient acetylide ion. More generally, the diversity of substrates and solvents used to measure proton transfer rates prevents significant comparisons and conclusions.

In view of these facts, and also of the scarcity of ionization data in non-aqueous solution, we have studied a variety of proton transfers in the same dipolar aprotic solvent, dimethyl sulphoxide (DMSO), and compared their rates and mechanisms with those obtained in water. DMSO is a good solvent for most organic substrates. However, it is a poor solvent for anionic nonpolarisable bases.[2] Its conjugate base is fairly stable under suitable experimental conditions.[13] Ion-pairing and homoconjugation may be neglected in dilute solutions of electrolytes.[14] A wide range of acidities is possible on account of a small autoprotolysis constant, $pK_{DMSO} = 33.3 \pm 0.3$.[15] Moreover, various p*K* values are readily available in this solvent.[2,16]

We are trying to set up a scale of kinetic acidities in this solvent for transfers to and from nitrogen (in ammonium salts), carbon (in acetylenic compounds), oxygen and sulphur (in alcohols and thiols), and phosphorus (in phosphonium salts). This paper deals with the acidity of the three acetylenes (1)—(3). The thermodynamic acidities of these substrates, ranging from 22.6 to 24.2 p*K* units (see below) were not accurately established, and our first task was to set up a pH and p*K* scale in moderately basic DMSO solution (pH 14—24). The kinetic acidities were studied using anhydrous DMSO solutions containing very small amounts (10^{-4}—10^{-2}M) of methylsulphinylmethanide (dimsyl) anion. Deprotonation rates were measured at 25 °C by means of ^1H and ^{13}C dynamic n.m.r. in solutions at equilibrium.

RC≡CH
(1) R = Ph
(2) R = $MeOCH_2$
(3) R = Me_2NCH_2

EXPERIMENTAL

Materials.—Dimethyl sulphoxide (Merck Uvasol) was left for 48 h over molecular sieves (Linde 3 Å), then distilled over calcium hydride under dry nitrogen at low pressure in an adiabatic fractionating column (1 m × 29 mm), with a reflux ratio of *ca.* 10, b.p. 27 °C at 0.3 mmHg. The water content of the purified solvent found by Karl Fischer

---

[1] Part 1, J-J. Delpuech and D. Nicole, *J.C.S. Perkin II*, 1974, 1025.

[2] C. D. Ritchie, 'Solute-Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1969, ch. 4.

[3] J. R. Jones, 'The Ionisation of Carbon Acids,' Academic Press, London, 1973; *Progr. Reaction Kinetics*, 1973, **7**, 1.

[4] M. Szwarc, A. Streitwieser, and P. C. Mowery, in 'Ions and Ion Pairs in Organic Reactions,' ed. M. Szwarc, Wiley, New York, 1974, vol. 2, ch. 2.

[5] E. F. Caldin and V. Gold, 'Proton-Transfer Reactions,' Chapman and Hall, Andover, 1975.

[6] R. P. Bell, 'The Proton in Chemistry,' Cornell University Press, Ithaca, 1959; E. F. Caldin, 'Fast Reactions in Solution,' Blackwell Scientific Publications, Oxford, 1964.

[7] D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965.

[8] F. A. Long and P. Ballinger, *J. Amer. Chem. Soc.*, 1959, **81**, 3148.

[9] E. A. Halevi and F. A. Long, *J. Amer. Chem. Soc.*, 1961, **83**, 2809.

[10] H. B. Charman, G. V. D. Tiers, M. M. Kreevoy, and G. Filipovich, *J. Amer. Chem. Soc.*, 1959, **81**, 3149.

[11] H. B. Charman, D. R. Vinard, and M. M. Kreevoy, *J. Amer. Chem. Soc.*, 1962, **84**, 347.

[12] R. E. Dessy, Y. Okuzumi, and A. Chen, *J. Amer. Chem. Soc.*, 1962, **84**, 2899.

[13] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1962, **84**, 866; 1965, **87**, 1345.

[14] E. J. King, 'Physical Chemistry of Organic Solvent Systems,' eds. A. K. Covington and T. Dickinson, Plenum Press, London, 1973, ch. 3.

[15] J. Courtot-Coupez and M. Le Demezert, *Compt. rend.*, 1968, **C266**, 1438; R. Stewart and J. R. Jones, *J. Amer. Chem. Soc.*, 1967, **89**, 5069.

[16] D. Dolman and R. Stewart, *Canad. J. Chem.*, 1967, **45**, 911.

titration was $<5 \times 10^{-3}$M. The acetylenic compounds (1) (Fluka; purum), (2) (Schuchardt Merck; 96%), and (3) (Aldrich; 97%) were distilled over molecular sieves under dry nitrogen in a Nester–Faust spinning band column (1 m), b.p. 143, 63, and 81 °C, respectively, and kept under nitrogen in a refrigerator. Indicators (4), (6), (7), and (10) (see Table 1) were Fluka products (puriss) used without further purification. Other indicators (5) (Aldrich), (8) (Aldrich; 99%), and (9) (Fluka; 97%) were recrystallized either from benzene or cyclohexane. Dimsyl anion in DMSO was prepared after Corey,[13] using sodium hydride (Koch–Light). Dimsyl anion (*ca.* 0.1M) was titrated with standardized aqueous sulphuric acid solution under argon, using a 1 ml portion diluted into 20 ml freshly doubly distilled water.

Solutions.—Stock solutions of DMSO, containing a measured quantity of sodium dimsyl and an indicator were freshly prepared before use in a glove-box under purified argon, freed from moisture, oxygen, and organic vapours by means of a liquid air trap and two columns filled with molecular sieves and BTS catalyst (B.A.S.F.). This solution was mixed with known quantities of an acetylene and diluted with pure DMSO to obtain the desired concentrations. The pH of these unbuffered solutions (acetylide : acetylenic acid molar ratio 10^{-4}—10^{-2}) was stable for 30 min. These solutions were handled immediately for spectroscopic measurements (u.v. and n.m.r.) in securely stoppered cells.

Spectrophotometric Measurements.—A Unicam SP 1800 spectrophotometer and a pair of 1 cm glass cells (Hellma 110-0S) with Teflon stoppers were used for all measurements. The substituted anilines and diphenylamines (4)—(10) were examined as indicators. All obey the Beer–Lambert law, which was not the case for 4,5-methylenephenanthrene (p*K* 20.0 [2,17]) used in a preliminary report,[18] thus leading to erroneous measurements. The molar extinction coefficients ε_0 of the anionic form were determined in DMSO containing an excess of dimsyl anion. Values are reported in Table 1.

TABLE 1

Absorption wavelengths, $\lambda_{max.}$, extinction coefficients, ε, and p*K* values of the indicators used in DMSO

Indicator	$\lambda_{max.}$/nm	ε	p*K*
2,4-Dinitroaniline (4)	540	13 200	14.80
2,5-Dichloro-4-nitroaniline (5)	460	26 700	16.16
2-Nitrodiphenylamine (6)	548	9 400	17.70
4-Nitroaniline (7)	467	32 000	19.24
3-Chlorodiphenylamine (8)	370	27 500	21.38
2,6-Dichloroaniline (9)	380	5 000	22.55
2,4-Dichloroaniline (10)	399	3 300	23.44

The ratio r_{AH} of the two forms AH and A^- of an indicator in an unknown solution was computed from its extinction coefficient ε or from the optical density D; $r_{AH} = [AH] : [A^-] = (\varepsilon_0 - \varepsilon)/\varepsilon = (D_0 - D)/D$.

First, an absolute p*K* scale was established for these indicators according to the stepwise method of Hammett. Pairs of overlapping indicators (A_H and B_H) were added successively to an identically buffered DMSO solution (of unknown pH), using dimsyl anion as base, and either phenols or the acetylenic substrates themselves as weak acids. pK_{BH} was derived from pK_{AH} by measuring the two corresponding ratios r_{AH} and r_{BH}, $pK_{BH} = pK_{AH} + \log(r_{BH}/r_{AH})$. Corrections for ionic activities cancel for these indicators, which are all of the same charge type. The relative p*K* scale thus obtained was anchored to the p*K* of 2,4-dinitroaniline, 14.8. This value was determined by Ritchie and Uschold[17] by means of a reversible glass electrode standardized at pH 3.

These values were used in turn to derive the pH of an unknown solution from $\text{pH} = pK_{AH} + \log r_{AH}$. Finally, the p*K* values of the acetylenes themselves were determined from the pH values at half-neutralization by dimsyl anion measured with the appropriate indicator (Table 3) in dilute solutions (10^{-2}M). The water and dimsyl concentrations (5×10^{-3}M) in such solutions were directly checked by Karl Fischer and acidimetric titrations. More concentrated solutions ($>5 \times 10^{-2}$M) led to erroneous p*K* values, presumably because of ion pairing. It is difficult to estimate the uncertainties in the p*K* values of the acetylenes and of the indicators used to determine them. The error is likely to increase for higher p*K* values because of the stepwise procedure used to measure them. The relative p*K* values of indicators not more than 2 p*K* units apart are known with an accuracy of *ca.* ±0.03 unit. Each p*K* interval of this size is subject to a random error of this same order of magnitude, so that we consider the total error as the quadratic mean, *i.e. ca.* 0.07 p*K* unit. The data in Tables 1 and 3 are significant only to the first decimal place.

^{1}H *N.m.r. Spectroscopy.*—The ^{1}H spectra were taken with a JEOL C 60-HL spectrometer at 60 MHz and 25 °C. AB_2 Type spectra of *NN*-dimethylprop-2-ynylamine (3) (Figure 1) and of 3-methoxypropyne (2) were analysed according to known procedures,[19] using the program LAOCOON3:[20] (2) δ_A 3.12, δ_B 3.19 (J_{AB} 2.2 Hz); (3) δ_A 3.43, δ_B 4.08 (J_{AB} 2.4 Hz). The δ_A shifts are slightly dependent on the concentration[21] of the acetylene as a result of autoassociation [δ_A 3.12, 3.08, and 3.06 for 0.37, 0.75, and 1.12M-(3) respectively]. Theoretical curves (with and without exchange) were obtained from a Texas Instruments 980 A minicomputer and a recorder, using the program EXCH14[22] (Figure 1). Values of τ_{BH}, the mean lifetime of one acetylene proton between two consecutive deprotonations, were thus measured as a function of pH. The indicator was present in the n.m.r. tube, and the concentration of its ionized form (10^{-5}—10^{-4}M) was often of the same order of magnitude as that of the other bases (10^{-4}—10^{-2}M). The pH of the solution is dependent on the indicator concentration, but its presence is immaterial as far as the deprotonation rate is concerned. This point was carefully checked as follows. Three indicator molarities (1.0, 2.0, and 3.2 × 10^{-4}M) were used for solutions of substrate (3) chosen as an example. Variable amounts of dimsyl anion were then added to each of these three solutions to obtain exactly the same pH value (21.2 ± 0.02); the three coalesced spectra could be exactly superimposed.

^{13}C *N.m.r. Spectroscopy.*—The ^{13}C spectra of non-enriched substrates were obtained from a Bruker HX-90 apparatus at 22.63 MHz. The 10 mm o.d. spinning tube contained a

---

[17] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, 1967, **89**, 1721; 1968, **90**, 2821.

[18] Preliminary report, J. M. Chrisment and J-J. Delpuech, *Tetrahedron Letters*, 1972, 521.

[19] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, p. 123.

[20] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 1964, **41**, 3863.

[21] J. C. D. Brand, G. Eglinton, and J. F. Morman, *J. Chem. Soc.*, 1960, 2526; R. E. Richards and J. V. Hatton, *Trans. Faraday Soc.*, 1961, **57**, 28; M. M. Kreevoy, H. B. Charman, and D. R. Vinard, *J. Amer. Chem. Soc.*, 1961, **83**, 1978.

[22] J-J. Delpuech and G. Serratrice, *Org. Magnetic Resonance*, 1972, **4**, 667.

thin capillary filled with [$^2H_6$]benzene, used both as a deuterium lock and as an external ^{13}C reference. The Fourier transform technique was found to be necessary and was achieved by means of a Nicolet 1805 computer and an additional Bruker pulse unit. A programming device for proton decoupling was used to produce periodic irradiation during a short waiting period before each interferogram to obtain coupled spectra keeping the Overhauser gain. In these conditions, 2 000 0.8 s scans of 8—16 K points over 1 200 Hz (resolution 0.15 Hz), using 30 μs radiofrequency pulses allow for a S : N ratio of *ca.* 40 and 15 for the DMSO spectrum (16 lines distributed over 4 quartets of quartets [23]) and for the doublet of phenylacetylene PhC≡^{13}CH, respectively. The coalescence of this doublet yielded values of the mean lifetime $\tau_{C_6H_5C_2H}$ of one acetylenic proton according to well known procedures.[23] As far as the coalescence of the DMSO quartets is concerned, the theory giving the mean lifetime τ_{DMSO} of one proton in one DMSO molecule has been explained previously.[23]

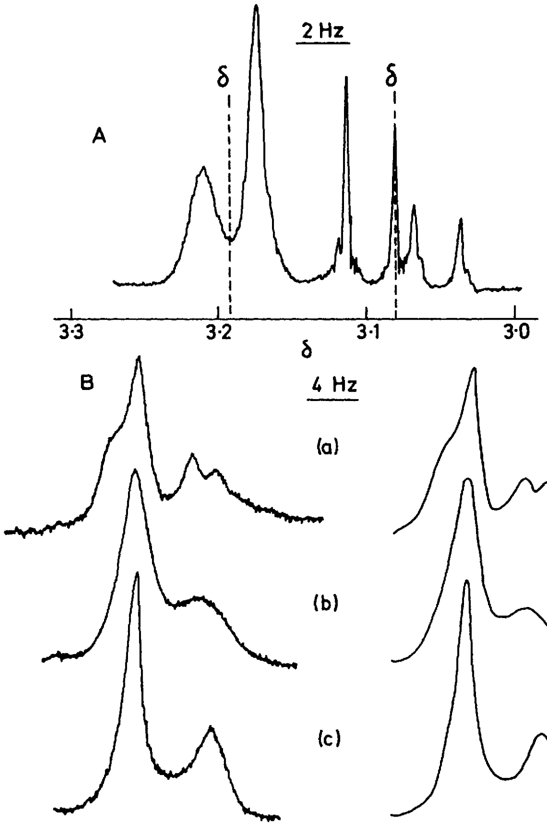

FIGURE 1 A, N.m.r. spectrum of *NN*-dimethylprop-2-ynylamine in DMSO at 25 °C and 60 MHz. B, Experimental (left) and theoretical (right) curves at pH (a) 21.66; (b) 21.96; and (c) 22.25; $1/\tau$ (a) 6.25; (b) 12.0; and (c) 25.5 s^{-1}

RESULTS

In water, only one deprotonation mechanism has been described, namely proton abstraction by hydroxide ion.[10,11] In DMSO, two mechanisms are possible. The attacking base may be either the conjugate acetylide ion, or the residual hydroxide ion [reactions (1) and (2)]. These two

$$BH + B^- \xrightarrow{k_1} B^- + HB \qquad (1)$$

$$BH + OH^- \xrightarrow{k_2} B^- + H_2O \qquad (2)$$

reactions give the kinetic law (3) where K_{BH} and K_{H_2O} are

$$1/\tau_{BH} = k_1[B^-] + k_2[OH^-] = (k_1K_{BH}[BH] + k_2K_{H_2O}[H_2O])/[H^+] \qquad (3)$$

the ionization constants of BH and H_2O respectively. The concentrations [BH] and [H_2O] are usually confused with the analytical concentrations themselves.

The contribution of the dimsyl anion ($DMSO^-$) to the deprotonation [equation (4)] may be thought to be negligible

$$BH + DMSO^- \xrightarrow{k_4} B^- + DMSO \qquad (4)$$

on account of the concentration of $DMSO^-$, much smaller than those of the acetylide and hydroxide ions. This point was actually demonstrated by measuring the rate constant of the reverse reaction from the ^{13}C lineshapes of DMSO and computing k_4 by equation (5). The corresponding contri-

$$k_4 = k_{-4}K_{BH}/K_{DMSO} \qquad (5)$$

bution to the numerator of equation (3), $k_4K_{DMSO} = k_{-4}K_{BH}$, is negligible compared to k_1K_{BH}[BH] and/or $k_2K_{H_2O}[H_2O]$, on account of the small values found for k_{-4} (*ca.* 10 l mol^{-1} s^{-1}). Details are now given for each substrate before the general discussion.

Three concentrations of *NN*-dimethylprop-2-ynylamine and, in each case, five pH values were used for coalescence, as shown in Table 2. A plot of $1/\tau_{BH}$ as a function of $1/[H^+]$ yields a straight line passing through the origin of co-ordinates (Figure 2). The least squares slopes p were computed assuming a zero intercept. A plot of p against acetylene concentration is also a straight line, as expected from equation (3). Its slope, $a = 1.84 \times 10^{-22}$ s^{-1} allows the rate constant of reaction (1) to be computed, $k_1 = a/K_{BH} = 2.92 \times 10^3$ l mol^{-1} s^{-1} at 25 °C. The contribution of reaction (2) to equation (3) is negligible within experimental error.

TABLE 2

pH and ($1/\tau_{BH}$) values in basic DMSO for various concentrations of *NN*-dimethylprop-2-ynylamine (pH indicator, 2,4-dichloroaniline)

[BH] = 0.37M		[BH] = 0.75M		[BH] = 1.12M	
pH	τ^{-1}_{BH}/s^{-1}	pH	τ^{-1}_{BH}/s^{-1}	pH	τ^{-1}_{BH}/s^{-1}
21.66	3.0	21.15	2.5	21.15	3.0
21.93	6.5	21.66	6.5	21.62	9.5
22.15	10.0	21.78	8.3	21.85	15.0
22.29	14.5	21.96	12.0	22.02	22.0
22.49	23.0	22.25	25.0		
		Slope (p/mol l^{-1} s^{-1})			
7.39×10^{-22}		13.89×10^{-22}		21.23×10^{-22}	

Simultaneously, we have observed the ^{13}C lines of DMSO, which remain sharp in this pH range (21—22). Adding massive quantities of dimsyl anion however results in the coalescence of each DMSO quartet (Figure 3). The concentration of the acetylene is kept in slight excess so as to

---

[23] J. Chrisment, J-J. Delpuech, and P. Rubini, *Mol. Phys.*, 1974, **27**, 1663 and references therein.

avoid leaving any dimsyl ion in the solution ($[DMSO^-]/[B^-] \leqslant 10^{-4}$), since the parallel proton transfer from DMSO to $DMSO^-$ is slightly faster than from DMSO to B^- : 22.1 [23]

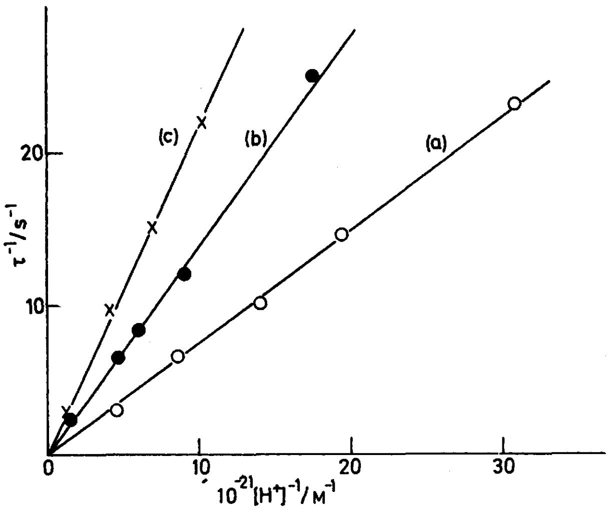

FIGURE 2 Plot of $(\tau_{Me_2NCH_2C\equiv CH})^{-1}$ *versus* $[H^+]^{-1}$ in basic DMSO at 25 °C for $[Me_2NCH_2C\equiv CH]$ 0.37 (a); 0.75 (b); and 1.12M (c)

against 6.59 l mol^{-1} s^{-1} at 25 °C. Two series of measurements were carried out using respectively [BH] = 0.75 and $[DMSO^-]$ = 0.72M in the first experiment, and 0.47 and 0.43M in the second. Two values of $1/\tau_{DMSO}$ were thus obtained, 4.8 and 2.8 s^{-1}, and, in turn, two values of k_{-4} as $1/\tau_{DMSO} = k_{-4}[B^-]$. Taking $[B^-]$ as 0.72 or 0.43M this gives

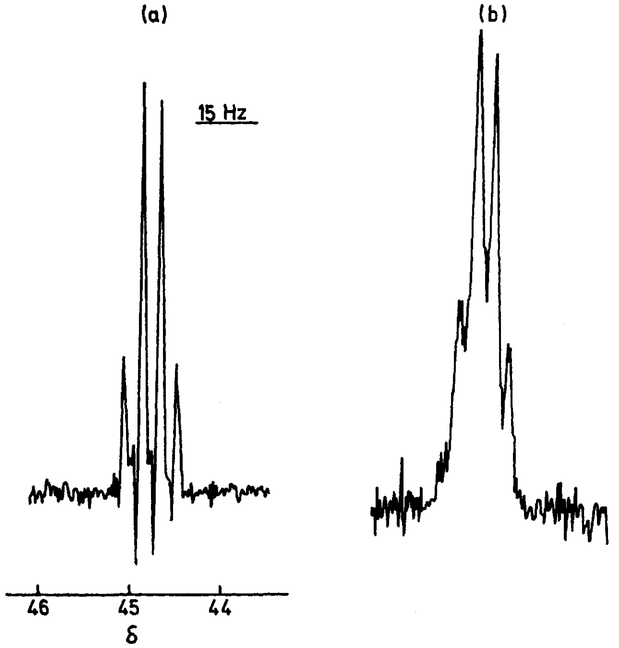

FIGURE 3 ^{13}C N.m.r. spectrum of one of the four quartets [23] of DMSO containing 0.75M-*NN*-dimethylprop-2-ynylamine, with no dimsyl (a) or 0.72M-dimsyl anion added (b)

k_{-4} = 6.66 and 6.51, *i.e.* 6.59 ± 0.08 l mol^{-1} s^{-1}. The rate constant k_4 of reaction (4) is then derived according to equation (5): $k_3 = 8.29 \times 10^9$ l mol^{-1} s^{-1}. The contribution of reaction (4) to reaction (3), $k_3K_{DMSO}/[H^+] = 4.15 \times 10$,[24] is therefore negligible, as expected.

Similar experiments were carried out with 3-methoxypropyne, giving $a = 1.24 \times 10^{-19}$ s^{-1} and k_1 3.93×10^4 l mol^{-1} s^{-1} at 25 °C. The ^{13}C DMSO lines began to broaden only after a massive addition of 1.07M-sodium dimsyl to a 1.09M solution of compound (2), for which $1/\tau_{BH} = 1.2$ s^{-1}.

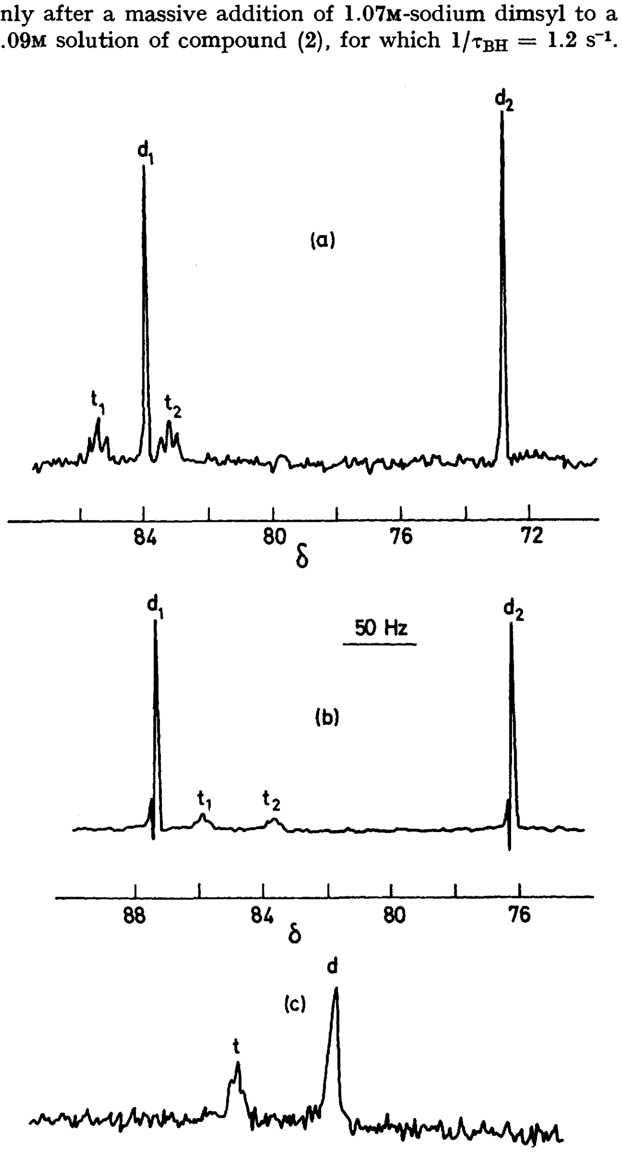

FIGURE 4 ^{13}C N.m.r. spectrum of the acetylene carbons of phenylacetylene PhC≡CH, either pure (a), or as a 2.73M solution in DMSO, with no dimsyl (b), or dimsyl anion ($2.5 \times 10^{-2}M$) added (c)

Rate constants k_{-4} and k_4 were derived from this value, k_{-4} 1.1, k_3 6.94×10^9 l mol^{-1} s^{-1} at 25 °C.

For phenylacetylene, the singlet for the acetylenic proton remained sharp after successive additions of dimsyl ion, showing that proton exchange takes place exclusively between like molecules of phenylacetylene through reaction (1). Non-decoupled ^{13}C n.m.r. was necessary to obtain k_1.

[24] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972, pp. 87, 347, and 360, and references therein.

$\equiv C$–H phenylacetylene yields a doublet[24] with two components 251 Hz apart from each other (Figure 4a). The resonance signal of Ph*C* is a doublet of triplets t_1 and t_2 (^2J 49, ^3J 5.5 Hz). The triplets often vanished under the experimental conditions used, on account of the exceptionally long relaxation time, 132 s,[25] and were rejected for accurate kinetic measurements. The chemical shifts of *C*H, and, to a lesser extent, of *C*Ph are solvent dependent, δ(*C*H) 78.41 and 81.68 p.p.m., δ(*C*Ph) 84.30 and 84.68, in the pure liquid or in a 0.9—2.7M solution in DMSO (Figures 4a and b, respectively). Because of the large frequency interval between exchanging sites, the fast exchange region only was used since the signal at coalescence is too diffuse to be distinguished from the baseline noise. In these conditions, the doublets d_1 and d_2 collapsed into a broad singlet d, and the triplets t_1 and t_2 into a unique triplet t, well apart from d (Figure 4c). The high rates thus obtained: $1/\tau_{\text{BH}} = 1.65$, 2.7, 6.55, and 15.0×10^4 s^{-1}, demanded in turn high concentrations of added dimsyl ion, 0.005, 0.01, 0.025, and 0.05M, respectively. The resulting solutions were therefore much more stable, thus allowing for spectrum accumulation to improve the signal : noise ratio. This explains why the *C*Ph doublet was rejected, in spite of its interestingly different time scale.

TABLE 3

Rate constants (l mol^{-1} s^{-1} at 25 °C) of proton abstraction from monsubstituted acetylenes

Substrate	p*K*	pH Range at coalescence	k_1	k_4	k_{-4}
Phenylacetylene (1)	22.6		2.92×10^6		
3-Methoxypropyne (2)	23.5	19.5—20.1	3.93×10^4	6.9×10^9	1.1
NN-Dimethylprop-2-ynylamine (3)	24.2	21—21.5	2.92×10^3	8.3×10^9	6.59

Phenylacetylide ion is yellow and no pH was measured in the coalescence range. The dimsyl concentrations were sufficiently large to assume a quantitative neutralization of the acetylenic proton. The acetylide concentration was thus identified with that of the added dimsyl anion [DMSO$^-$]. The aforementioned values of $1/\tau_{\text{BH}}$ fit an approximately linear correlation with respect to [DMSO$^-$], whose slope yields the rate constant for reaction (1): $k_1 = 2.92 \times 10^6$ l mol^{-1} s^{-1} at 25 °C.

Finally, no modification of the ^{13}C DMSO lines was observed even when 1.05M-sodium dimsyl was added to a 1.19M solution of phenylacetylene. This shows that $k_{-4} \ll 1.0$ l mol^{-1} s^{-1}, while k_4 is presumably diffusion limited.

DISCUSSION

The predominant mechanism for deprotonation of acetylenes (1)—(3) involves proton transfer with the conjugate base itself. Rate constants k_1 are increasing with higher acidities of the acetylenic proton (Table 3). This result was not self-evident since a stronger acidity of the leaving proton is accompanied by a weaker basicity of the attacking conjugate base. Better still, a linear correlation between log k_1 and p*K* is observed [equation (6)] with the three pairs of data available (mean deviation $\pm$0.08). The activation free energy $\Delta G^\ddagger$ of reaction (1)

$$\log k_1 = -1.884\,\text{p}K + 48.995 \qquad (6)$$

is thus decreasing along this series of acetylenic compounds 1.884 times as fast as the free energy ΔG accompanying the ionization equilibrium $\text{BH} + \text{DMSO} \rightleftharpoons \text{B}^- + \text{DMSO} \cdots \text{H}^+$. As $\Delta\Delta G^\ddagger = \Delta G(\text{TS}) - \Delta G(\text{BH}) - \Delta G(\text{B}^-)$ and $\Delta\Delta G = \Delta G(\text{B}^-)$, relationship (7) is obtained

$$|\Delta G(\text{TS})| > 2|\Delta G(\text{B}^-)| \qquad (7)$$

where TS represents the symmetrical transition state of reaction (1). (Transfer itself, with a one-half probability,

$$\text{RC}{\equiv}\text{C}^{\delta-} \cdots \text{H}^{\delta+} \cdots {}^{\delta-}\text{C}{\equiv}\text{CR}$$

is achieved by a spontaneous collapse of the central proton to either of the two negative systems, the whole process consisting in a proton jump along a double well potential curve.) Charge separation in TS must be larger for the more acidic acetylenes. The positive charge on the bridging proton thus becomes closer to unity on going from substrate (1) to (3). A large energy decrease may then arise from the solvation of the positive pole (H$^+$) of TS by the basic DMSO molecules, while small energies are involved in the solvation of either the free acetylide anions or the negatively charged acetylide parts of the TS. The stabilization brought both by charge delocalization and solvation is reasonably expected to be more important in TS than in the two free acetylide anions, thus accounting for inequality (7).

We notice that the rate constants k_1 and k_{-4}, but not k_4, are independent of the absolute p*K* values, *i.e.* of the p*K* of the indicator chosen to anchor our pH scale. We may however check the validity of the k_4 values, by observing that their ratio for substrates (2) and (3) is again independent of our pH scale. This ratio, 1.2 $\pm$ 0.5, is close to unity, within experimental error (arising mainly from p*K* measurements). On the other hand, the corresponding ratio of the k_{-4} values is equal to 6.0. These results show that variations Δlog k_4 are nearly zero, and variations Δlog k_{-4} equal the corresponding Δp*K*. In a log *k*-p*K* Eigen plot, this means that k_{-4} follows the Brönsted law of exponent unity, while k_4 is diffusion-limited. The absolute k_4 values shown in Table 3 fit this prediction nicely, since they are close to 10^{10} l mol^{-1} s^{-1}.

Conversely, this means, according to equation (5), that $K_{\text{BH}}/K_{\text{DMSO}} \simeq 10^{10}$, or that $\text{p}K_{\text{BH}} = 23.3 \pm 0.3$ when $k_{-4} \simeq 1$ l mol^{-1} s^{-1}. The p*K* of 3-methoxypropyne ($k_{-4} = 1.1$ l mol^{-1} s^{-1}) is therefore predicted as 23.3, in agreement with the experimental value of 23.5. Phenylacetylene is conveniently predicted more acidic than 3-methoxypropyne, since reverse of reaction (4) becomes too slow to be measured on the n.m.r. time scale. The

---

[25] G. C. Levy, *J.C.S. Chem. Comm.*, 1972, 47.

decrease in p*K* on going from compound (3) to (1) is confirmed by measuring the frequency of the ≡CH stretching vibration for solutions of the acetylenes in carbon tetrachloride and dimethyl sulphoxide. It is well known that the basicity of DMSO is responsible for hydrogen bonding with acetylenic protons.[26] Effectively, the absorption band observed at 3 310 cm^{-1} for all acetylenes in carbon tetrachloride is shifted towards lower wavenumbers in DMSO. The shift is largest (120 cm^{-1}) for phenylacetylene as expected from its higher acidity. Referring all the measured shifts to the largest one, the difference is 0 (phenylacetylene), 10 (3-methoxypropyne), and 17 cm^{-1} (*NN*-dimethylprop-2-ynylamine).

Our consistent set of data invites confidence in both our kinetic parameters and p*K* values. It leads us to reject a recently published value of 28.8 for the p*K* of phenylacetylene in DMSO,[27] which is also in contrast with the approximate value of the so-called MSAD scale.[28] Other kinetic considerations, to be developed in a later publication, make such a high value even more unlikely. Phenylacetylene would be more basic than the residual water itself (p*K* 28.2),[15] and the contribution of reaction (2) to equation (3) would then become predominant, as it can be observed when using another set of more basic acetylenes.[29]

All n.m.r. spectra were recorded on spectrometers of the Groupement Régional de Mesures Physiques de l'Académie de Nancy-Metz. We thank M. Diter for technical assistance. The glove-box was built by M. Clement and the i.r. spectra were recorded by M. Gross.

[6/891 *Received*, 10*th May*, 1976]

---

[26] C. Agami, *Bull. Soc. chim. France*, 1969, 2183; C. Agami and M. Caillot, *ibid.*, p. 1990.

[27] 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.

[28] Ref. 4, p. 170; E. M. Kosower, 'An Introduction to Physical Organic Chemistry,' Wiley, New York, 1968.

[29] J. Chrisment and J-J. Delpuech, unpublished results.