material (8%) and 84.1 mg (50%) of the aldehyde (identical with an authentic sample): ^{1}H NMR ($CDCl_3$) δ 1.30 (10 H, br s), 1.70 (2 H, m), 2.00 (2 H, m), 2.40 (2 H, br t), 5.00 (2 H, m), 5.81 (1 H, m), 9.78 (1 H, t); IR ($CHCl_3$) 2695 (CH=O), 1715 (C=O) cm^{-1}.

Aldehyde 3b:[4] yield 85%; mp 187–190 °C; ^{1}H NMR (CCl_4) δ 1.4 (6 H, t, J = 7 Hz), 1.65–1.85 (2 H, m), 3.45 (1 H, br t), 3.5–3.68 (1 H, m), 3.85 (3 H, s), 4.4 (4 H, q, J = 7 Hz), 4.8 (1 H, br s), 5.2 (1 H, br s), 9.7 (1 H, s); MS, m/z 328 (M$^+$).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, le Ministère de l'Education du Gouvernement du Québec, and The Upjohn Co. for financial assistance.

Registry No. 3 (R = Bn), 98652-05-2; 3 (R = Et), 98757-08-5; 4 (R = Bn), 98652-04-1; 4 (R = Et), 98717-43-2; $CH_3(CH_2)_7NO_2$, 629-37-8; $CH_3CH_2CH(NO_2)CH(OH)CH_3$, 5447-99-4; $CH_2{=}CH(CH_2)_9NO_2$, 40244-98-2; octanal (2,4-dinitrophenylhydrazone derivative), 1726-77-8; cyclohexanone (2,4-dinitrophenylhydrazone derivative), 1589-62-4; acetone (2,4-dinitrophenylhydrazone derivative), 1567-89-1; benzaldehyde (2,4-dinitrophenylhydrazone derivative), 1157-84-2; 2-hydroxy-3-pentanone (2,4-dinitrophenylhydrazone deriv), 98652-06-3; octanal, 124-13-0; nitrocyclohexane, 1122-60-7; cyclohexanone, 108-94-1; 2-nitropropane, 79-46-9; acetone, 67-64-1; nitrophenylmethane, 622-42-4; benzaldehyde, 100-52-7; 2-hydroxy-3-pentanone, 5704-20-1; 10-undecenyl aldehyde, 112-45-8.

Gas-Phase Basicity of Ring-Substituted Phenylacetylenes

Franco Marcuzzi, Giorgio Modena,* and Cristina Paradisi

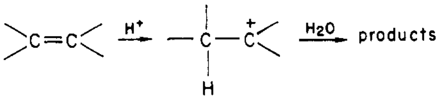
Centro Meccanismi di Reazioni Organiche del C.N.R., Istituto di Chimica Organica, 35131 Padova, Italy

Carlo Giancaspro and Maurizio Speranza

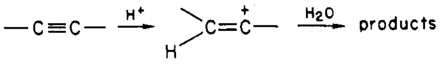
Istituto di Chimica Nucleare del C.N.R., 00016 Roma, Italy

Received March 25, 1985

The reactivity of carbon–carbon double and triple bonds toward electrophiles has been the subject of numerous investigations and discussions.[1-3] A particularly interesting feature of these reactions concerns the relative reactivity of double vs. triple bonds bearing equal substituents, which varies greatly (over the 10^{-2}–10^8 range) depending mainly on the electrophile and, to minor extents, on the substituents and solvent.[4,5] In particular, the acid-catalyzed hydration of alkenes and alkynes has been studied in great detail. The reaction proceeds according to the $A_{SE}2$ mechanism, which involves as first and rate-limiting step the protonation of the π-system to give carbenium ion intermediates; these are rapidly trapped by a water molecule (eq 1 and 2). Interestingly, in contrast to the still widespread, and somewhat erroneous, notion that vinyl cations are intermediates of much higher energy than the corresponding saturated ions, analogously substituted alkynes and alkenes have comparable reactivities toward the proton.[5] This behavior is in contrast with that of other electrophiles, such as Br_2, which are orders of magnitude more reactive toward the double bond relative to the triple bond. In reactions with the proton, it has also been observed that the reactivity of alkynes is somewhat more sensitive to ring-substitution than that of alkenes.[6,7] Thus, arylacetylenes give slightly more negative slope parameters, ρ^+, than the corresponding styrene derivatives in correlations of the rates of protonation in aqueous sulfuric acid solutions with σ^+ constants. The magnitude of these ρs depends on the acid concentration,[6] their absolute values becoming larger as the acidity of the medium is increased. Finally, analysis of these reactions according to the Bunnett and Olsen treatment[8] has indicated the absence of major differential solvent effects in the protonation of triple and double bonds in the acidity range accessible for kinetic determinations.[6]



(1)



(2)

Table I. Gas-Phase Basicities (GB) of Phenylacetylenes 1

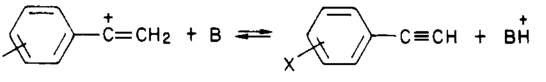
compd	GB,[a] kcal mol^{-1}	compd	GB,[a] kcal mol^{-1}
1a	192.2	1e	190.8
1b	202.3	1f	186.6
1c	196.8	1g	187.4
1d	192.5	1h	184.2

[a] Data calculated relative to GB(NH_3) = 196.4 kcal mol^{-1}.

An extension of the study of the protonation behavior of double and triple bonds to the gas phase is obviously of extreme interest because gas-phase data, free of solvent and counterion effects, are a "clean" measure of the intrinsic properties of the species involved. A recent article reporting on the gas-phase basicities (GB) of ring-substituted styrenes[9] has prompted us to determine the GBs of a series of analogously substituted phenylacetylene derivatives. These data provide a direct comparison of the energetics involved in the protonation of the double and triple bonds in the gas phase at low pressure in the absence of any intramolecular interaction. A brief discussion of the substituent effects, assessed from the ρ^+ parameter, on the thermodynamic gas-phase basicity as well as on the kinetics of protonation in aqueous solutions is also presented.

Results

The gas-phase basicities (GB) of ring-substituted phenylacetylenes 1 have been determined by measuring, in an FTICR spectrometer, equilibrium constants for reaction 3, where B are suitable reference bases of known basicity. The data are reported in Table I.



(3)

1a-h

1a, X=H; 1b, X=4-OCH$_3$; 1c, X=4-CH$_3$; 1d, X=4-F; 1e, X=4-Cl; 1f, X=3-F; 1g, X=3-Cl; 1h, X=3-CF$_3$

Plots of GB data against the Brown–Hammett σ^+ substituent constants for substituted phenylacetylenes 1,

---

(1) Schmid, G. H.; Garratt, D. G. "The Chemistry of Functional Groups. Supplement A. The Chemistry of Double-Bonded Functional Groups"; Patai, S., Ed.; Wiley-Interscience: London, 1977; Part 2, p 725.

(2) Nowlan, V. J.; Tidwell, T. T. *Acc. Chem. Res.* **1977**, *10*, 252.

(3) (a) Schmid, G. H. "The Chemistry of the Carbon–Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978; Part 1, Chapter 8. (b) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979; Chapter 4.

(4) Yates, K.; Schmid, G. H.; Regulski, T. W.; Garratt, D. G.; Leung, H. W.; McDonald, R. *J. Am. Chem. Soc.* **1973**, *95*, 160.

(5) Melloni, G.; Modena, G.; Tonellato, U., *Acc. Chem. Res.* **1981**, *14*, 227.

(6) Modena, G.; Rivetti, F.; Scorrano, G.; Tonellato, U. *J. Am. Chem. Soc.* **1977**, *99*, 3392.

(7) Allen, A. D.; Chiang, Y.; Kresge, A. J.; Tidwell, T. T. *J. Org. Chem.* **1982**, *47*, 775.

(8) Bunnett, J. F.; Olsen, F. P. *Can. J. Chem.* **1966**, *44*, 1899, 1917.

(9) Harrison, A. G.; Houriet, R.; Tidwell, T. T. *J. Org. Chem.* **1984**, *49*, 1302.

0022-3263/85/1950-4973$01.50/0

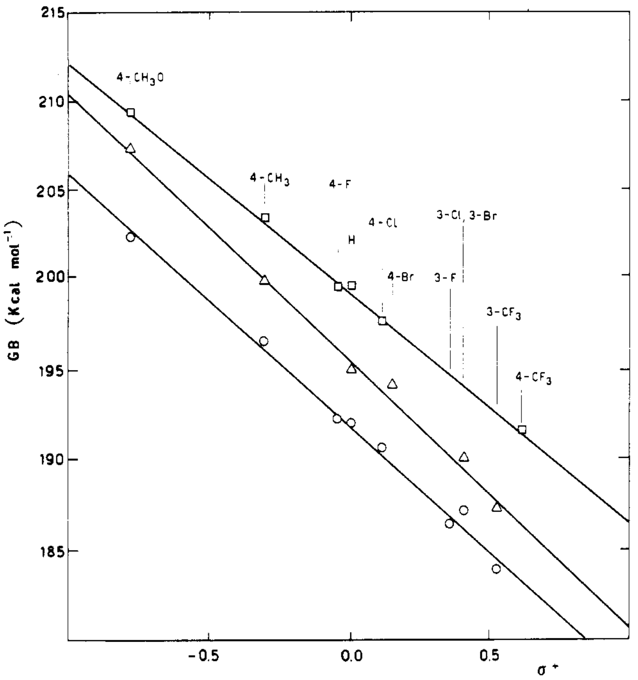
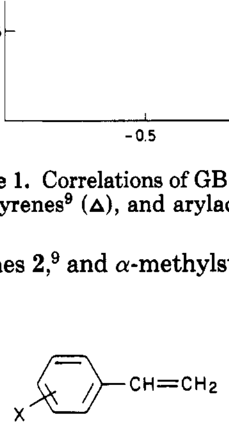
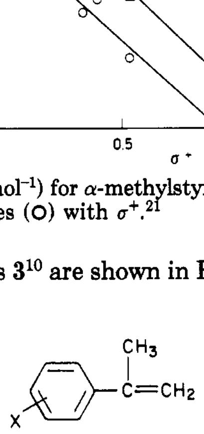


Figure 1. Correlations of GB (kcal mol^{-1}) for α-methylstyrenes[10] (□), styrenes[9] (△), and arylacetylenes (○) with σ^+.[21]

styrenes 2,[9] and α-methylstyrenes 3[10] are shown in Figure 1.



2

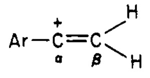


3

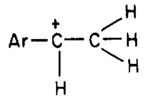
Discussion

Substituted phenylacetylenes have three sites where protonation can potentially occur; the triple bond, the benzene ring, and, for specific X, the substituent. A recent mass spectrometric investigation has demonstrated that the site of protonation of phenylacetylene under chemical ionization conditions is the triple bond.[11] Under our equilibrium conditions protonation can also be safely assumed to take place on the triple bond in view of the following facts: (i) the GB data correlate linearly with the σ^+ parameters, without significant deviations[12] (Figure 1); (ii) the GB of phenylacetylene (192.2 kcal mol^{-1}) is significantly higher than that of toluene (185.2 kcal mol^{-1}),[12] and ethylbenzene (186.1 kcal mol^{-1});[13] and (iii) the ρ values for arylacetylenes and for the styrenes series are equal within the experimental error. We believe that the above observations provide good evidence that both styrenes and arylacetylenes are protonated on the aliphatic π-system under equilibrium conditions. The GB data are therefore representative of the relative basicities of double and triple bonds in the gas phase.

In the gas phase substituted phenylacetylenes are consistently less basic than the corresponding styrenes by a few kcal mol^{-1}. These observations are in agreement with recent results of a PES study,[14] which has shown that styrenes have consistently lower ionization energies than the corresponding arylacetylenes. Substituent effects measured in gas-phase protonation equilibria are very similar for styrenes and arylacetylenes. The ρ^+ values obtained from GB vs. σ^+ plots[15] are −10.0 and −10.7 for 1 and 2, respectively, i.e., equal within experimental error. This result is in contrast to the expectation that lower intrinsic basicities should bring about an enhanced sensitivity to ring-substitution and thus an increase in the absolute value of ρ^+. A trend of this sort has been recognized in the ρs for protonation equilibria involving α-methylstyrenes 3 ($\rho^+ = -9.2$) and styrenes, 2 ($\rho^+ = -10.7$).[9] In the case under examination, however, other stabilizing interactions could contribute to disperse the positive charge of the cationic species and their relative weights could likely be more significant for α-arylvinyl cations 4 than for α-arylethyl cations 5. Possibly, one such interaction could be due to hyperconjugation of the C_β–H bonds. Moreover, other factors such as bond lengths and polarizability of the C_α–C_β bond, could contribute to level down the electron demand from the aryl substituent in 4. Interestingly, theoretical calculations predict that substituent effects are inherently similar for trivalent carbenium ions and vinyl cations,[16] in agreement with our experimental results.



4



5

The thermodynamic basicity of double and triple bonds in solution cannot be evaluated because of fast reactions of the protonated species with the solvent.

A direct evaluation of solvent effects on these protonation equilibria is, therefore, precluded. One can, however, attempt to compare substituent effects and relative thermodynamic basicities in the gas phase with kinetic data relevant to protonation in aqueous sulfuric acid solutions. This is in part justified by evidence that the activated complex for proton-transfer reactions in aqueous solutions closely resembles the final product (α-Brönsted values[17] and solvent kinetic isotope effects).[18]

Once allowance is made for these difficulties, the data in the gas phase and in solution appear to be in reasonably good agreement. The rates of hydration of equally substituted styrene–arylacetylene pairs are indeed of the same order of magnitude, relative reactivities falling within the 1–5 range. The ρ values are also similar, −3.0 for the styrenes and −3.5 for the arylacetylenes (ρ values extrapolated to the reference state ($H_0 + \log H^+) = 0$)[6].

The fact that arylacetylenes have lower gas-phase basicities than styrenes and yet comparable solution reactivity toward the proton suggests the possibility that α-arylvinyl cations 4 have larger solvation energies than the corresponding α-arylethyl cations 5. Interestingly, this expected

---

(10) (a) Data taken from ref 10b and recalculated relative to GB(NH_3) = 196.4 kcal mol^{-1}. (b) Hartman, K. N., Lias, S.; Ausloos, P.; Rosenstock, H. M.; Schroyer, S. S.; Schmidt, C.; Martinsen, D.; Milne, A. "A Compendium of Gas-Phase Basicity and Proton Affinity Measurements"; U.S. Department of Commerce, Washington, DC, 1979; NBSIR 79-1977.

(11) Apeloig, Y.; Franke, W.; Rappoport, Z.; Schwarz, H., Stahl, D. *J. Am. Chem. Soc.* **1981**, *103*, 2770.

(12) (a) An example of a shift in the site of protonation being revealed by a deviation from the GB vs. σ^+ correlation is found in ref 11b. (b) Lau, Y. K., Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452.

(13) Aue, D. H.; Bowers, M. T. "Gas-Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 9.

(14) (a) Ajò, D.; Casarin, M.; Tondello, E.; Marcuzzi, F.; Modena, G., submitted for publication; (b) Levin, R. D.; Lias, S. G. "Ionization Potential and Appearance Potential Measurements". 1971–1981, NSRDS-NBS 71, 1982.

(15) ρ^+ is obtained by multiplying the slope of the GB vs. σ^+ plot by the factor 1000/2.303RT.

(16) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Org. Chem.* **1977**, *42*, 3004.

(17) Noyce, D. S.; Schiavelli, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 1020.

(18) Noyce, D. S.; Schiavelli, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 1023.

difference in solvation energies is not reflected in the kinetic parameter $\phi_\ddagger$, which measures the solvation requirements of the transition states, leading to **4** and **5**, relative to their respective neutral precursors.[6] However, it appears that the $\phi_\ddagger$ parameter is mostly sensitive to specific solvation interactions such as hydrogen-bonding, and, therefore, it is probably not suited to reveal small differences due to other terms which may contribute to the overall energy of solvation.[19] One could speculate that specific electrostatic interactions with the counterion and/or cavitation energy terms, not influencing $\phi_\ddagger$, could favor the smaller vinyl cation and contribute to overcome the intrinsic lower basicity of the triple relative to the double bond.

To summarize, the following conclusions can be drawn: (i) arylacetylenes are less basic in the gas phase than the corresponding styrene derivatives by a few kcal mol^{-1}; (ii) protonation of the double and triple bonds in these systems under equilibrium conditions in the gas phase is equally sensitive to ring-substitution, and (iii) a reasonably good match is observed between the protonation behavior in the gas phase and in solution so that major differences in the solvation energies of α-arylvinyl and α-arylethyl cations are excluded.

Experimental Section

Compound **1a** was a commercial product and was purified by fractional distillation at reduced pressure.

Compounds **1b–h** were prepared by literature methods,[20] in some cases with minor modifications, and purified according to standard procedures. Final purification of compound **1b** was achieved by preparative GLC.

The purity of all the samples was checked by ^{1}H NMR and GLC techniques before running the FTICR experiments.

The FTICR experiments were performed on a commercial Nicolet FT-MS 1000 with the magnetic field set at 2 T. The proton affinities were determined by using the braketing technique and/or, where possible, equilibrium measurements. The compounds were introduced via two different leak valves and their pressures (not corrected) were measured with a Granville-Phylips 280 Bayard Alpert ion gauge. The typical pressure in the experiments was 3 × 10^{-6} torr with a neutral ratio of about 1.

Reference bases used (and their GB values in kcal mol^{-1}) are 4-cyanopyridine (202.4), *sec*-Bu_2O (200.8), *i*-Pr_2O (198.0), acetophenone (197.2), NH_3 (196.4), *n*-Bu_2O (195.5), *t*-BuOMe, (194.1), *n*-Pr_2O (193.7), anisole (192.5), 3-pentanone (192.7), *i*-PrCOMe (192.6), PhCHO (192.2), ethylacetate (192.1), Et_2O (191.7), 2-butanone (191.2), THF (190.5), methyl acetate (189.5), PhCN (188.2), acetone (188.0), dioxane (185.0), and Me_2O (183.4).

The protonated reference bases were isolated after a convenient delay by sweeping out all the undesidered ions with two consecutive double resonance events.

The reactions between the protonated bases and the samples were followed at different trapping times and, where possible, the equilibrium constants were determined. The estimated average uncertainty in these determinations is ±0.2 kcal mol^{-1}.

Acknowledgment. We acknowledge the collaboration of Dr. Roberto Gabrielli of the Servizio FT-MS of the Area di Ricerca del C.N.R., Roma.

Registry No. **1a**, 536-74-3; **1b**, 768-60-5; **1c**, 766-97-2; **1d**, 766-98-3; **1e**, 873-73-4; **1f**, 2561-17-3; **1g**, 766-83-6; **1h**, 705-28-2.

---

[19] Taft, R. W.; Wolf, J. F.; Beauchamp, J. L.; Scorrano, G.; Arnett, E. M. *J. Am. Chem. Soc.* **1978**, *100*, 1240.

[20] (a) Overberger, C. G.; Saunders, J. H. "Organic Syntheses"; Wiley: New York, 1953, Collect. Vol. III, p 204. (b) Mesnard, D.; Bernadou, F.; Miginiac, L. *J. Chem. Res., Synop.* **1981**, 270. (c) Dehmlow, E. V.; Lissel, M. *Tetrahedron* **1981**, *37*, 1653. (d) Gorgues, A.; Le Coq, A. *Tetrahedron Lett.* **1976**, 4723.

[21] Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

Application of ^{13}C NMR Spectroscopy to Acyclic Stereochemical Analysis

James K. Whitesell*

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

Bernhard Hildebrandt

Department of Chemistry, Philipps University—Marburg, D-3550, Marburg, West Germany

Received April 18, 1985

In the past ten years, ^{13}C NMR spectroscopy has begun to evolve as one of the most powerful tools at the disposal of the synthetic chemist for unraveling stereochemical questions. For example, the difference in congestion experienced by a substituent that is either endo or exo on a bicyclic array is of such a magnitude that it is often possible to decide the stereochemical orientation of a substituent with a high degree of confidence even when only one of the two possible diastereomers is in hand.[1] This situation contrasts very markedly with that in acyclic systems where generally a cyclic derivative is prepared before stereochemical analysis is carried out spectroscopically. This approach is often rationalized on the basis that conformational analysis in complicated, acyclic systems would be so imprecise that reliable predictions could not be made. We suspect that this latter opinion is invoked in the majority of cases without an actual analysis of the situation. As a markedly contrasting example, we would like to provide a relatively simple conformational analysis of the alcohols **1** and then, on the basis of this analysis, to derive predictions for the expected ^{13}C chemical shifts.[2]

There are two dominant influences on the chemical shift of a carbon: (1) the number and nature of the atoms attached either α or β; (2) the steric (and to a lesser extent, electronic) interactions with atoms that are situated γ (as well as those that are more remote). The spacial and bonding relationships between atoms that are either α or β to one another are invariant with rotation about σ bonds, so long as bond angles are not also changed. Thus, the differences observed between diastereomers result from the interaction of γ as well as more remote substituents. The shift perturbation due to γ substituents has been extensively discussed.[3] The magnitude of these differences is often large as can be seen by comparison of the chemical shifts for the three diastereomeric alcohols **1a–c**,[4] where the chemical shift differences between the lowest and highest field C-3, C-5 methyl groups as well as the methylenes (C-2 and C-6) are both δ 3.7. This is certainly a sufficiently large difference that, with all isomers in hand, a reasonable prediction in a mono- or polycyclic system could be reliably made. It occurred to us that the number of reasonable conformations in such systems might not be as large as would be at first anticipated. If this were indeed the case then the effect of γ substituents observed in rigid bicyclic arrays where spacial relationships are well defined

---

[1] For example, see: Whitesell, J. K.; Matthews, R. S. *J. Org. Chem.* **1977**, *42*, 3878.

[2] It is perhaps important to point out that these predictions were arrived at in the absence of the correlation between spectral data and stereochemistry and, therefore, did not evolve intentionally or otherwise along lines so as to arrive at a reasonable fit between prediction and experiment. In addition, the assignment of stereochemistry to **1a–1c** is based on the chemistry of their formation and symmetry arguments, not the spectral data.[4]

[3] See: Gorenstein, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 2254 and references cited therein.

[4] Hoffmann, R. W.; Zeiss, H. J.; Ladner, W.; Tabche, S. *Chem. Ber.* **1982**, *115*, 2357.