Tetrahedron Letters, Vol. 34, No. 37, pp. 5903-5906, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Substituent Effect on Gas Phase Basicity of 1-Phenylpropyne. Thermodynamic Stability and Resonance Demand of 1-Phenylpropenyl Cations

Shinjiro KOBAYASHI,* Takatsugu MATSUMOTO, Hiroshi TANIGUCHI, Masaaki MISHIMA,[†]*
Mizue FUJIO,[††] and Yuho TSUNO[††]*

Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812, Japan

[†]Institute for Molecular Science, Okazaki 444, Japan

[††]Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

Abstract: Gas phase basicities have been determined for l-phenylpropynes by measurement of proton transfer equilibrium with a pulsed ion cyclotron resonance spectrometer. The LArSR analysis of the substituent effect gave a ρ of -13.3 and an r of 1.12. The r value satisfies the relationship of "resonance demand-carbocation stability" derived for ordinary sp^2-hybridized benzylic carbocations as well as that of phenylacetylene.

Numerous efforts have been done to clarify properties of vinyl cations from the various standpoints in the last twenty five years.[1-3] Recently we could elucidate the thermodynamic aspect of vinyl cations based on gas phase basicities (GB) of the corresponding acetylenes determined by measuring proton transfer equilibrium, where it was found that the substituent effect on the stability of 1-phenylvinyl cation was described successfully in terms of the LArSR Eq. (1) with a ρ of -14.1 (kcal mol^{-1} σ^{-1}) and an r of 1.21.[4] The ρ value is equal to that for

$$\delta\Delta G^0 = \rho\ (\ \sigma^0 + r\,\Delta\,\bar{\sigma}_R^+\ ) \qquad (1)$$

ordinary sp^2-hybridized benzylic carbocations, indicating the same response of the stability of l-phenylvinyl cation to the substituent polarity as that of benzylic carbocations. The r value was found to be intermediate between that of α-phenylethyl and benzyl cations. This feature of l-phenylvinyl cation satisfies the linear relationship between the r values and the stability of the parent carbocations (ring substituent = H) observed for a series of benzylic carbocations, i.e., the more stable carbocations have the smaller r value in magnitude and vice versa.[5, 6] From these results, it has been inferred that π-delocalization mechanism in the phenylvinyl cation is not of specific mode but is merely characterized by a unique position of 1.21 in a continuous spectrum of resonance demands of benzylic carbocations. It is particularly of interest to examine the dependence of resonance demand on the stability of vinyl cations for understanding further intrinsic nature of vinyl cations. In this study, we have therefore studied the substituent effect on the stability of l-phenylpropenyl cation which must be more stable than l-phenylvinyl cation by the β-methyl substituent. Furthermore, this would provide a new insight into whether the hyperconjugative interaction between the vacant p-orbital and the C_β-CH_3 bond plays an important role for the determination of the stability of vinyl cations.[7]

Gas phase basicities have been determined for a series of 1-phenylpropynes by measurement of proton transfer equilibrium (2) using more than two suitable reference bases for each derivative with a homemade pulsed ion cyclotron resonance mass spectrometer as described previously.[8] Gas phase basicity of 1-phenylbutyne has also been measured to determine the effect of β-substituent. Since gas phase basicities of reference bases used for the present measurement are available in literature, the free energy changes of the equilibrium (2) can be converted into the relative GB values to the unsubstituted 1-phenylpropyne. Those are summarized in Table 1 together with the corresponding values of α-methylstyrenes and phenylacetylenes.

(2)

The GB value of the unsubstituted 1-phenylpropyne is found to be 1.8 kcal mol^{-1} (1 cal = 4.184 J) higher than that of phenylacetylene, indicating that the introduction of the methyl group at the β-position increases the stability of the conjugate acid ion, 1-phenylpropenyl cation. Similarly, 1-phenylbutenyl cation is more stable by 3.3 kcal mol^{-1} than 1-phenylvinyl cation, since the GB value of 1-phenyl-1-butyne is 194.9 kcal mol^{-1}. The effect of the β-alkyl group on the stability of phenylvinyl cation appears to be larger than that observed for ordinary sp^2-hybridized carbocations, e.g., the stability of α-ethyl-α-methylbenzyl cation is only 0.4 kcal mol^{-1} higher than α-cumyl cation and their resonance demands is equal.[12] This trend is also in accord with our recent results

Table 1. Relative Gas Phase Basicities of 1-Phenylpropynes(**1**), Phenylacetylenes(**2**) and 1-Methylstyrenes(**3**)

	ΔGB / kcal mol^{-1}		
Substituent	**1**[a]	**2**[b]	**3**[c]
p-OMe	11.8	13.0	10.5
p-OMe-m-Cl	7.9	9.1	6.7
p-Me	4.7	5.5	4.1
m-Me	1.9	2.2	1.8
p-Cl	-0.5	0.1	-0.5
m-F	-5.1	-5.6	-5.1
m-Cl	-4.5	-5.1	-4.7
m-CF$_3$	-6.5	-6.6	-6.2
3,5-F$_2$	-8.4		-8.5
H	0.0	0.0	0.0
	(193.4)[d]	(191.6)[d]	(199.1)[d]

a) This work at 343 K. b) Refs. 4 and 9. c) Ref. 10. d) GB values in absolute scale, calculated relative to GB(NH$_3$)=195.6 kcal mol^{-1}.[11]

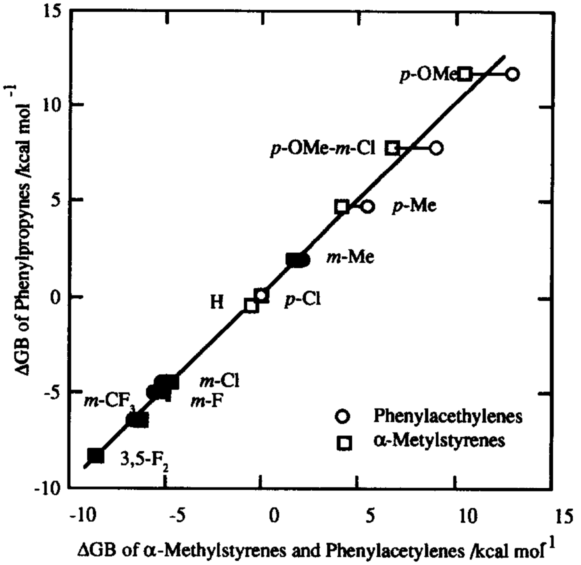

Fig. 1. Plots of relative gas phase basicities of 1-phenylpropynes against the corresponding α-methylstyrenes and 1-phenylacetylenes.

of solvolysis. The solvolysis rate of 1-phenyl-2-methylpropenyl triflate in 80 % aqueous EtOH[13]is ten fold faster than the corresponding 1-phenylvinyl triflate[14], while α,α-di-alkylbenzyl chlorides have similar or even slower rate than α-cumyl derivatives.[15] These results imply two possibilities, hyperconjugation and/or field/inductive effect . The hyperconjugative interaction between the vacant p-orbital and the C_β-CH_3 bond might not play a major part, to explain the large stabilization by the ethyl group. Therefore, transmission of field/inductive effect through the double bond of vinyl cations to the cationic center seems to be intrinsic as similar as the one through aromatic ring observed in the dissociation of substituted benzoic acids.

In Fig. 1 are plotted the relative GB values of 1-phenylpropynes against those of α-methylstyrenes and phenylacetylenes. Meta substituents (dark points in Fig. 1) and para-π acceptors provide an excellent linear relationship with a slope of unity against both GB values of α-methylstyrenes and phenylacetylenes, suggesting that there is no essential difference in the response to the substituent field/inductive effects among these three systems. On the contrary, para π-donor substituents give systematic deviations from the line mentioned above, i.e., the stronger π-donor substituents show the greater deviations. Such deviation patterns are observed whenever there is difference in resonance demand between two systems of interest.[16] The upward deviations of para π-donors observed for the plots versus α-methylstyrenes in Fig. 1, therefore, would be indicative of exalted resonance stabilization by these substituents in the 1-phenylpropenyl cation system compared with that in the α-cumyl one. In addition, since the GB values of α-methylstyrenes have been correlated excellently with σ^+ substituent constants, the substituent effect on the GB value of phenylpropyne is expected to have greater resonance demand than unity for α-cumyl cation. For the plots versus the GB values of phenylvinyl cations, one can find an opposite situation, i.e., para π-donor substituents deviate downward from the line of the meta and para-π acceptor substituents, suggesting reduced resonance stabilization by these substituents in the 1-phenylpropenyl cation compared with that in the phenylvinyl cation. Consequently, it is inferred from Fig. 1 that the resonance demand of 1-phenylpropenyl cation must be intermediate between that of phenylvinyl cation (1.21) and α-cumyl cation (1.00). Indeed, application of LArSR Eq. (1) to the substituent effect for stability of 1-phenylpropenyl cations gives an r of 1.12 and a ρ of -13.3 (kcal mol^{-1} σ^{-1}). The ρ value is equal to that of α-cumyl cation and 1-phenylvinyl cation as expected from Fig. 1, indicating the same response to the substituent field/inductive effects for these three systems regardless of the different stability of the respective parent carbocations (ring substituent = H). This is in accord with our previous observations for a series of sp^2-hybridized benzylic carbocation.[5, 6, 17, 18] Regarding the change in the r value with the system, we have found in previous studies that its change in magnitude is related to the change of the intrinsic stability of parent carbocation of respective systems, i.e., the more unstable carbocation has the greater r value.[5, 6] The magnitude of the r value of 1-phenylpropenyl cation seems to be also reconciled with the variation of the r value depending on the stability of the parent carbocations (ring substituent = H). Indeed, there exists a good linear relationship between resonance demands (r) and stability (ΔG^0(H)) of the parent carbocations including α-

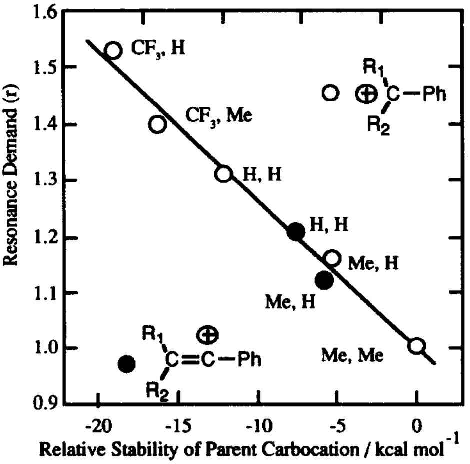

Fig. 2. Relationship between resonance demand (r) and stabilities of carbocations

phenylvinyl cations as shown in Fig. 2. This strongly supports our conclusion that the resonance demand is a function of structure of a carbocation, and suggests that π-delocalization mechanism in vinyl cations is not characteristic mode but is merely characterized by a specific position in a continuous spectrum of resonance demands of a series of carbocations stabilized by an α-aryl group.[4, 9)] Further study should be required for clarify the effect of β-alkyl group on stability of vinyl cations.

The authors gratefully acknowledge support for this research by a Grant-in-Aid for Scientific Research from Ministry of Education, Science and Culture, and by the Joint Studies program of the Institute for Molecular Science.

REFERENCES

1. Stang, P. J. ; Rappoport, Z.; Hanack, M; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York. 1979.
2. Rappoport, Z. *Reactive Intermediates;* Plenum Press: New York. 1983; Vol. 3; Chap. 7.
3. Marcuzzi, F.; Modena, G.; Paradisi, C. *J. Org. Chem.* **1985,** *50,* 4973-4975.
4. Mishima, M.; Ariga, T.; Fujio, M.; Tsuno, Y.; Kobayashi, S.; Taniguchi, H. *Chem. Lett.* **1992**, 1085-1088.
5. Mishima, M.; Inoue, H.; Fujio, M.; Tsuno, Y. *Tetrahedron Lett.* **1990,** *31,* 685-688.
6. Mishima, M.; Inoue, H.; Fujio, M.; Tsuno,Y. *Tetrahedron Lett.* **1989,** *30,* 2101-2104.
7. Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Amer. Chem. Soc.* **1977,** *99,* 5901-5909.
8. Mishima, M.; Fujio, M.; Tsuno, Y. *Mem. Fac. Sci., Kyushu Univ., Ser. C* . **1984,** *15(1),* 365-374.
9. Mishima, M.; Ariga, T.; Fujio, M.; Tsuno, Y.; Kobayashi, S.; Taniguchi, H. *Mem. Fac. Sci., Kyushu Univ., Ser. C* . **1988,** *16(2),* 217-224.
10. Mishima, M.; Usui, S.; Fujio, M.; Tsuno, Y. *Nippon Kagaku Kaishi.* **1989,** 1262-1268.
11. Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref: Data* **1984,** *13,* 695-808.
12. Nakamura, H.; Mishima, M.; Fujio, M.; Tsuno, Y. unpublished result.
13. Kobayashi, S.; Matsumoto, T.; Taniguchi, H. unpublished result.
14. Stang, P. J.; Hargrove, R. J.; Dueber, T. E. *J. Chem. Soc. Perkin 2,* **1977,** 1486 -1490.
15. Orlovic, M.; Kronja, O.; Humski, K.; Borcic, S.; Polla, E. *J. Org. Chem.*, **1986,** *51,* 3253-3256.
16. Tsuno, Y., Fujio, M.; Goto, M.; Murata, A.; Mishima, M. *Tetrahedron,* **1987,** *43,* 307-316.
17. Mishima, M.; Usui, S.; Fujio, M.; Tsuno, Y. *Nippon Kagaku Kaishi.* **1989,** 1269-1274.
18. Mishima, M.; Usui, S.; Arima, K.; Fujio, M.; Tsuno, Y. *Chem. Lett.*, **1987,** 1047-1051.

(Received in Japan 19 February 1993; accepted 21 May 1993)