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Substituent Effects on the Gas Phase Acidity of Phenylacetylenes and Benzyl Alcohols

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The gas phase acidities of *meta*- and *para*-substituted phenylacetylenes and benzyl alcohols were determined by measuring equilibrium constants of proton transfer reactions using a FT-ICR spectrometer. The gas phase acidities of phenylacetylenes and benzyl alcohols are related linearly to those of benzoic acids with a slope of unity. Since the CH_2 group of benzyl alcohol prevents a direct π-electron interaction between substituents and the negative charge at the oxygen atom, the existence of these linear relationships suggests that σ^{o} parameters best describe the substituent effects in all three systems. Indeed, the acidities of phenylacetylenes and benzoic acids correlate with σ^{o} values determined in the gas phase. The theoretical calculations of these acidities at MP2/6-311++G**//B3LYP/6-311++G** level of theory could reproduce the substituent effects observed experimentally. The optimized geometries and the elctrostatic charges computed using the CHELPG scheme of Breneman for the conjugate anions of all three acid systems also indicate that there is no π-delocalization of the negative charge into the benzene ring.

Since carbanions are the most widely used reactive intermediates for the formation of carbon–carbon bonds in organic synthesis,[1] the stabilities of carbanions have been extensively investigated by acidity measurements in solution and in the gas phase, and by theoretical calculations.[2–11] Of particular interest are acidities of acetylene compounds, because an acetylenic proton can be replaced by metal ions to form metal acetylides as useful synthetic intermediates.[1] Substituent effects on the acidity of acetylenic hydrogens, however, have not been studied well because alkynes are too weakly acidic to be deprotonated under conventional conditions. Although Bordwell and co-workers constructed a scale of acidities of weakly acidic compounds in dimethyl sulfoxide, only a few acetylene compounds were reported.[11] Kinetic data on the deprotonation of carbon acids are relatively easier to obtain than equilibria data,[12,13] but the former are often complicated by ion-pairing, internal return, and other mechanistic complexities. It was found that alkyl groups decrease the rates of deprotonation of alkynes and that, for a limited number of compounds, a plot of $\log k$ against σ^{*} is linear, but the whole series of phenylacetylenes does not fit simply on a single Hammett plot.[12,14] Thus, substituent effects on the acidity of acetylenic hydrogens are not understood well. Accordingly, we have examined acidities of substituted phenylacetylenes in the gas phase where there are no difficulties arising from solvation, ion-pairing, and other mechanistic complexities. Gas phase acidities of benzyl alcohols were also determined in this study. A comparison between benzyl alcohols and phenylacetylenes is particularly useful in the study of substituent effects on phenylacelylenes because a direct resonance effect in the benzyl alcohols is not possible. In addition, DFT calculations were carried out to gain further information on properties of acetylides.

$$\begin{aligned} &XC_6H_4C{\equiv}CH + C_6H_5C{\equiv}C^- \\ &\quad = XC_6H_4C{\equiv}C^- + C_6H_5C{\equiv}CH \end{aligned} \tag{1}$$

$$\begin{aligned} &XC_6H_4CH_2OH + C_6H_5CH_2O^- \\ &\quad = XC_6H_4CH_2O^- + C_6H_5CH_2OH. \end{aligned} \tag{2}$$

Results and Discussion

Gas Phase Acidity. The gas-phase acidities were determined by measuring the equilibrium constants of the reversible proton-transfer reactions between the investigated compounds and a reference acid of known acidity (3) using a Fourier transform ion cyclotron resonance mass spectrometer. The free energy changes ($\Delta\Delta G^{\circ}_{\mathrm{acid}}$) for respective proton transfer equilibria and the selected $\Delta G^{\circ}_{\mathrm{acid}}$ values[15] for the present compounds are summarized in Table 1 along with reference acids (A_oH) with their $\Delta G^{\circ}_{\mathrm{acid}}$. The substituent effects on the acidity of phenylacetylene and benzyl alcohol are summarized in Table 2.

$$AH + A_o{}^- = A^- + A_oH. \tag{3}$$

Figure 1 shows a plot of the relative acidities of phenylacetylenes against those of the corresponding benzoic acids as a standard set of substituent effects in the gas phase.[16,17] There is a good linear relationship between these two reactions (slope = 1.04, $R^2 = 0.998$). The slope of unity indicates that the response of the stability of the phenylacetylide to the change of substituent is the same as that in the carboxylate anion. An excellent linear correlation is also found between acidities of benzyl alcohols and phenylacetylenes, as shown in Fig. 2 (slope = 0.98, $R^2 = 0.996$).

In the benzyloxide, the negative charge cannot be delocalized into the benzene ring through resonance interaction be-

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Table 1. Free Energy Changes of Proton Transfer Eequilibrium and Gas Phase Acidities in kJ/mol

Acids	Reference acids [$\Delta G^\circ{}_{\mathrm{acid}}$]$^{a)}$	$\Delta\Delta G^{\circ b)}$	Selected $\Delta G^\circ{}_{\mathrm{acid}}$
p-$NO_2C_6H_4C\equiv CH$	p-$CF_3C_6H_4NH_2$ [1447.7]	14.6	
	m-$FC_6H_4NH_2$ [1480.7]	−15.9	
	p-$CF_3C_6H_4C\equiv CH$ [1479.9]	−15.5	1464.0
p-$CF_3C_6H_4C\equiv CH$	m-$FC_6H_4NH_2$ [1480.7]	−0.8	
	o-$FCC_6H_4NH_2$ [1486.6]	−7.9	
	p-$NO_2C_6H_4C\equiv CH$ [1464.0]	15.5	1479.9
m-$ClC_6H_4C\equiv CH$	o-$FC_6H_4NH_2$ [1486.6]	6.7	
	p-$FC_6H_4NH_2$ [1493.7]	−0.8	1492.9
p-$ClC_6H_4C\equiv CH$	p-$FC_6H_4NH_2$ [1493.7]	0.8	
	m-$ClC_6H_4CH_2OH$ [1494.5]	−0.4	
	p-$ClC_6H_4CH_2OH$ [1497.0]	−4.6	1494.5
m-$FC_6H_4C\equiv CH$	p-$FC_6H_4NH_2$ [1493.7]	3.8	
	$C_6H_5NH_2$ [1502.5]	−3.3	1498.3
$C_6H_5C\equiv CH$	$C_6H_5NH_2$ [1502.5]	12.6	
	p-$MeC_6H_4NH_2$ [1506.7]	8.4	
	CH_3COCH_3 [1516.3]	−0.8	
	$C_6H_5CH_2OH$ [1380.3]	−4.2	
	CH_3CN [1529.7]	−16.7	1515.0$^{c)}$
p-$NO_2C_6H_4CH_2OH$	m-$CF_3C_6H_4NH_2$ [1462.7]	2.5	
	m-$ClC_6H_4NH_2$ [1471.1]	−5.4	
	m-$FC_6H_4NH_2$ [1480.7]	−13.8	1465.7
p-$CF_3C_6H_4CH_2OH$	m-$FC_6H_4NH_2$ [1480.7]	0.8	
	o-$FC_6H_4NH_2$ [1486.6]	−2.9	1484.1
m-$CF_3C_6H_4CH_2OH$	m-$FCC_6H_4NH_2$ [1480.7]	5.9	
	o-$FC_6H_4NH_2$ [1486.6]	−0.4	1486.6
3,5-$F_2C_6H_3CH_2OH$	o-$FC_6H_4NH_2$ [1486.6]	1.3	
	p-$FC_6H_4NH_2$ [1493.7]	−4.6	1488.7
m-$ClC_6H_4CH_2OH$	p-$ClC_6H_4C\equiv CH$ [1494.5]	0.4	
	$C_6H_5NH_2$ [1502.5]	−6.7	1494.9
p-$ClC_6H_4CH_2OH$	p-$FC_6H_4CN_2$ [1493.7]	3.3	
	p-$FC_6H_4CH_2OH$ [1498.7]	−5.4	1497.0
m-$FC_6H_4CH_2OH$	p-$ClC_6H_4C\equiv CH$ [1494.5]	4.6	
	$C_6H_5NH_2$ [1502.5]	−3.3	1498.7
p-$FC_6H_4CH_2OH$	$C_6H_5NH_2$ [1502.5]	1.3	
	CH_3COCH_3 [1516.3]	−9.2	1503.7
$C_6H_5CH_2OH$	$C_6H_5C\equiv CH$ [1515.0]	4.2	
	CH_3COCH_3 [1516.3]	1.7	
	$CH_3CO_2CH_3$ [1527.6]	−9.2	1518.4$^{d)}$
p-$MeOC_6H_4CH_2OH$	CH_3COCH_3 [1516.3]	2.9	
	CH_3CN [1529.7]	−10.5	1519.2
p-$MeC_6H_4CH_2OH$	$C_6H_5C\equiv CH$ [1515.0]	7.5	1522.6

a) Acidity of reference compounds. b) Free energy changes of respective proton transfer equilibria. c) 1518.4 $\mathrm{kJ\,mol^{-1}}$ given in Ref. 16. d) 1520.5 $\mathrm{kJ\,mol^{-1}}$ given in Ref. 16.

cause of the insulating effect of the methylene group between the deprotonation site and the benzene ring. Consequently, the substituent effect on the acidity of benzyl alcohol is best described by the σ^{o}-parameter in the gas phase. The p-nitro group with a strong π-electron-withdrawing capability conforms to the linear correlation between the acidities of phenylacetylenes and benzyl alcohols; this suggests that the substituent effects on the acidity of phenylacetylene are also best described by the σ^{o}-parameter, i.e., the negative charge in the phenylacetylide is not delocalized into the nitro group at the *para* position by a direct π-interaction.

The similarity of substituent effects among these three systems suggests further that the acidities of benzoic acids in the gas phase also correlate with the σ^{o} parameters. Indeed, Fig. 3 shows excellent correlations of the acidities of these systems with the standard substituent constants, $\sigma^{\mathrm{o}}{}_{(\mathrm{g})}$, determined from gas-phase substituent effects on the stability of carbocations,[18] giving the ρ values[19] of 10.6 ($R^2 = 0.996$), 10.4 ($R^2 = 0.991$), and 10.3 ($R^2 = 0.993$) for phenylacetylene, benzyl alcohol, and benzoic acid, respectively.

In these correlations, somewhat modified $\sigma^{\mathrm{o}}{}_{(\mathrm{g})}$ values were needed for p-F, m-F, and p-Cl. This suggests that a different set of substituent constant values for such substituents may be necessary for analysis of the substituent effects of anionic systems. Such differences in the substituent effect between cation and anion systems may arise from the different contributions of the polarizability effect in the two systems, since the polarizable subsituent stabilizes both anion and cation.[20] However,

Table 2. Relative Gas-Phase Acidities (in kJ mol^{-1}) of Phenylacetylenes, Benzyl Alcohols, and Benzoic Acids and σ^{o} Substituent Constants in the Gas Phase

Subst.	Phenylacetylene	Benzyl alcohol	Benzoic acid[a)]	$\sigma^{o}_{(gas)}$[c)]
p-MeO		−1.3	−2.9	−0.10
p-Me	−4.6[b)]	−4.2	−4.6	−0.13
H	0.0	0.0	0.0	0.00
p-F		14.6	12.1	0.25 (0.20)
m-F	18.0	19.7	15.9	0.34 (0.26)
p-Cl	20.1	21.3	18.0	0.25 (0.30)
m-Cl	21.3	23.4	19.7	0.36
m-CF_3		31.8	30.5	0.50
p-CF_3	34.7	34.3	32.2	0.56
p-NO_2	50.6	52.7	49.0	0.80
3,5-F_2		29.3		0.453

a) Ref. 20. *p*-NH_2; −10.5, *m*-Me; −2.9, *p*-$COCH_3$; 23.4, *p*-CHO; 29.7, *m*-CN; 42.7, *p*-CN; 45.2, *m*-NO_2; 45.2, 3,5-$(CF_3)_2$; 60.7 are also given. b) M. L. Chabinyc and J. I. Brauman, *J. Am. Chem. Soc.*, **122**, 5371 (2000). c) σ^{o} values determined for the gas phase substituent effects of carbocation stabilities, Ref. 18. Values in parentheses are used for the present analysis of the anion systems, see text.

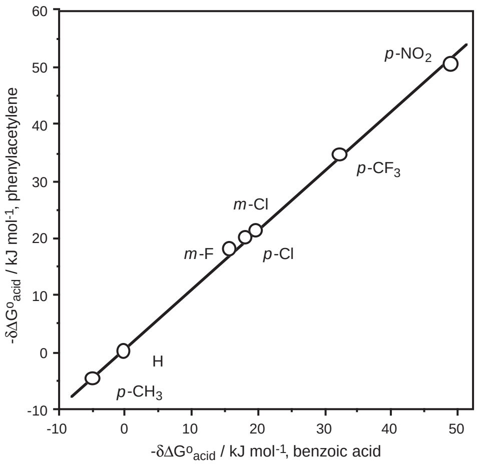

Fig. 1. Plot of the observed $-\delta\Delta G^{\circ}_{acid}$ values for phenylacetylenes vs benzoic acids.

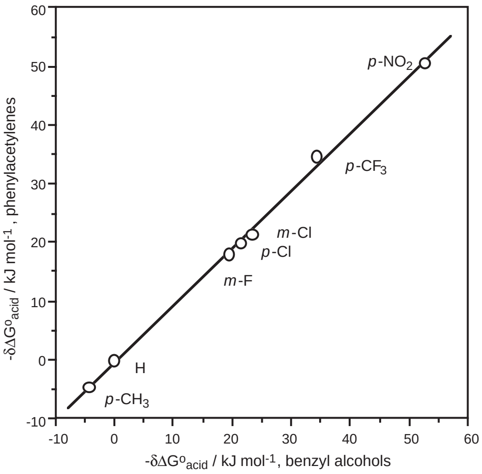

Fig. 2. Plot of the observed $-\delta\Delta G^{\circ}_{acid}$ values for phenylacetylenes vs benzyl alcohols.

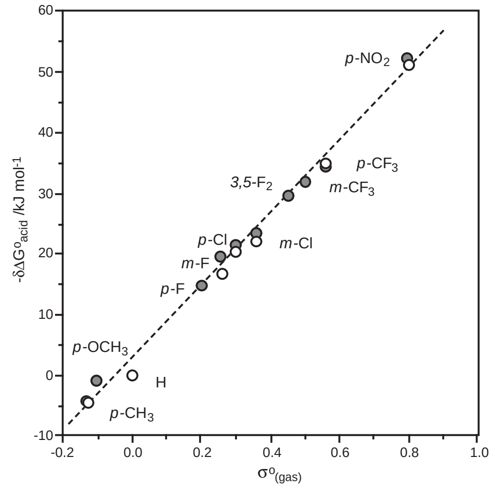

Fig. 3. Plot of the observed $-\delta\Delta G^{\circ}_{acid}$ values against $\sigma^{o}_{(gas)}$ for phenylacetylenes (open circles) and benzyl alcohols (closed circles).

the *m*-Cl group has the same effect in both systems. Further studies are clearly needed to clarify the reasons for the change of the $\sigma^{o}_{(g)}$ value with the system.

That the acidities of benzoic acids are linearly correlated with $\sigma^{o}_{(g)}$ may be surprising, because the corresponding reaction in aqueous solution is the standard reaction for the Hammett's σ values, in which the resonance effects of *para* π-donors are enhanced slightly compared to that involved in the σ^{o} substituent constants.[21] For example, the σ_p value of *p*-MeO is more negative than that of *p*-Me, while for σ_p^{o}, the reverse is true. The experimental acidities are apparently consistent with σ_p^{o} rather than with σ_p as pointed out by Kebarle and McMahon previously.[22] This conclusion is consistent with Wiberg's calculations that there is a remarkably good linear relationship between the calculated gas-phase acidities of benzoic acids and phenylacetic acids[23] in which the CH_2 group separates the benzene ring from the carboxyl group,

Table 3. Calculated Thermodynamic Parameters (ΔE, ΔH°, ΔG°, ΔS°)$^{a)}$ at B3LYP/6-311++G**//B3LYP/6-311++G** for Deprotonation of Phenylacetylenes, Benzyl Alcohols, and Benzoic Acids

Acids	ΔH°	ΔG°	ΔS°	ΔE(MP2)$^{b)}$	$\Delta H^\circ{}_{(W)}{}^{c)}$	$\Delta G^\circ{}_{obs}$
X in $XC_6H_4C{\equiv}CH$						
p-OMe	1557.3	1524.3	110.6	1587.7		
p-Me	1552.3	1520.0	107.5	1584.3		1519.6
m-Me	1549.3	1520.9	95.8	1582.6		
H	1546.8	1514.2	108.4	1580.6		1515.0
p-F	1536.8	1506.2	103.3	1570.7		
p-Cl	1528.4	1497.5	104.2	1565.5		1494.5
m-F	1528.4	1495.8	109.2	1565.4		1498.3
m-Cl	1524.2	1492.0	108.8	1561.8		1492.9
m-CF_3	1514.6	1482.0	109.2	1549.7		
p-CF_3	1506.7	1476.1	102.9	1547.7		1479.9
m-CN	1504.6	1472.3	108.4	1539.9		
p-CN	1493.3	1461.1	108.4	1536.6		
m-NO_2	1501.2	1468.6	109.6	1538.9		
p-NO_2	1477.0	1445.6	105.0	1531.8		1464.0
X in $XC_6H_4CH_2OH$						
p-OMe	1531.2	1502.9	94.8	1586.2		
p-Me	1530.9	1503.3	92.5	1587.0	1548.9	1522.6
m-Me	1530.5	1504.6	85.8	1585.7		
H	1527.2	1499.5	92.9	1583.6	1544.3	1518.4
p-F	1514.2	1486.6	92.5	1570.7	1531.3	1503.7
p-Cl	1507.5	1479.5	95.0	1564.0	1526.7	1497.0
m-F	1511.7	1483.2	94.1	1566.5	1527.6	1498.7
m-Cl	1505.8	1477.0	95.8	1564.4	1525.1	1494.9
m-CF_3	1494.9	1466.9	95.0	1552.3		1486.6
p-CF_3	1492.9	1465.2	93.3	1549.8	1512.1	1484.1
m-CN	1486.2	1457.3	96.2	1547.2	1499.1	
p-CN	1482.8	1453.5	97.5	1545.2	1502.9	
m-NO_2	1476.1	1449.3	89.5	1539.3	1500.0	
p-NO_2	1469.8	1442.6	91.2	1539.3	1500.0	1465.7
3,5-F_2	1494.1	1466.9	90.8	1551.0		
X in XC_6H_4COOH						
p-NH_2	1436.3	1403.7	109.3	1463.2	1427.2	1407.0
p-OMe	1425.8	1393.5	108.1	1457.7	1457.7	1396.2
p-Me	1422.6	1392.0	102.5	1459.4	1425.1	1397.9
m-Me	1420.0	1385.7	115.1	1458.5	1423.8	1396.2
H	1416.7	1384.9	107.5	1455.6	1421.3	1393.3
p-F	1403.7	1371.9	107.5	1442.6	1408.3	1381.1
p-Cl	1399.1	1366.5	109.2	1438.5	1404.6	1374.9
m-F	1398.7	1366.9	107.5	1438.5	1404.2	1377.4
m-Cl	1394.5	1362.3	107.9	1436.4	1401.6	1373.6
m-CF_3	1384.5	1352.3	107.5	1424.2	1389.9	1362.7
p-CF_3	1381.6	1348.9	109.2	1423.0	1389.1	1361.5
m-CN	1374.0	1342.2	107.1	1414.2	1380.3	1350.6
p-CN	1371.1	1338.9	107.9	1412.9	1379.9	1348.1
m-NO_2	1370.3	1338.0	108.4	1412.1	1380.3	1348.1
p-NO_2	1363.1	1330.9	108.4	1410.4	1376.5	1344.3

a) ΔE, ΔH°, and ΔG° in $kJ\,mol^{-1}$, ΔS° in $J\,mol^{-1}\,K^{-1}$. The thermodynamic quantities of the proton are 3.7 $kJ\,mol^{-1}$, 6.2 $kJ\,mol^{-1}$, -26.3 $kJ\,mol^{-1}$, and 108.8 $J\,mol^{-1}\,K^{-1}$ for *E*, *H*, *G*, and *S*, respectively. b) ΔE at MP2/6-311++G**//B3LYP/6-311++G**. c) Calculated at MP2/6-311++G**//MP2/6-311+G*, Refs. 23 and 24.

i.e., as for the benzyl alcohol system, σ^o parameters are appropriate here also. Accordingly, the resonance effect associated with σ values in aqueous solution, compared with that associated with σ^o values, is enhanced. The effect may be considered to be due to solvent effects on the neutral benzoic acids, i.e., the hydrogen-bonding interaction between aqueous solvent and the carbonyl group of neutral benzoic acids assists the resonance interaction between the π-donor at the *para* position and the carboxyl group.[22] The importance of such solvent effects on resonance effects in solution was previously noted by Taft.[17,20]

Calculated Acidities. The acidities of all systems were calculated at the B3LYP/6-31++G** level of theory. Vibrational normal mode analyses were performed at the same level to ensure that each optimized structure was a true minimum on the potential energy surface, and to calculate the thermal corrections needed to obtain the Gibbs free energies. Using geometries optimized at the B3LYP/6-311++G** level, a single point calculation was also carried out at MP2/6-311++G**. These results are given in Table 3 along with calculated acidities of benzyl alcohols and benzoic acids at the higher MP2/6-311++G**//MP2/6-311++G* level in the literature.[23,24]

The B3LYP calculated acidities ($\Delta G^\circ_{\rm acid}$) for phenylacetylenes are generally within 4 kJ/mol of the observed acidities except for the *p*-NO_2 derivative, but the calculated values for benzoic acids and benzyl alcohols are consistently about 8 and 17 kJ/mol too small, respectively. Although the calculated acidities at MP2/6-311++G**//MP2/6-311++G* for benzoic acids and benzyl alcohols give significantly better agreement, the acidities ($\delta\Delta E_{\rm acid}$) relative to the respective unsubstituted derivatives calculated at MP2/6-311++G**//B3LYP/6-311++G** are in satisfactory agreement with the observed acidities as follows: $\delta\Delta E_{\rm acid} = a\ \delta\Delta G^\circ_{\rm acid}({\rm obs})$ where $a = 0.95$ ($R^2 = 0.990$), 0.95 ($R^2 = 0.988$, ex. *p*-NO_2), and 0.95 ($R^2 = 0.996$) for phenylacetylene, benzyl alcohol, and benzoic acid systems, respectively. The calculated substituent effects, $\delta\Delta E_{\rm acid}$, show that there are good linear correlations among these three systems with a slope of unity.

$$\delta\Delta E_{\rm acid}(\text{phenylacetylene}) = 1.02\delta\Delta E_{\rm acid}(\text{benzoic acid}) - 0.8 \quad R^2 = 0.992 \tag{4}$$

$$\delta\Delta E_{\rm acid}(\text{benzyl alcohol}) = 0.94\delta\Delta E_{\rm acid}(\text{benzoic acid}) + 0.7 \quad R^2 = 0.991. \tag{5}$$

Closer examination of calculated acidities indicates that the *p*-methoxy derivative is a slightly stronger acid than the *p*-methyl derivative in the benzyl alcohol and benzoic acid systems, a conclusion in agreement with the experimental results and the $\sigma^{\rm o}$ parameters. On the contrary, the calculated acidities for the phenylacetylene system show the opposite order. The acid-weakening effect of *p*-OMe, however, is smaller than that expected from the $\sigma_{\rm p}$ parameters. Such small differences in the acidity calculated at the present level of theory would not be appropriate for further discussion. Thus, the calculated acidities support the conclusion derived from the experimental acidities that these acidity systems can be regarded as a $\sigma^{\rm o}$ system.

In addition, it is found that the change of bond lengths within the benzene ring upon ionization is quite small, except for C1C2 and C1C6 in the phenylacetylene system, indicating that there is no distinct trend in the bond lengths to show a contribution of π-delocalization of the negative charge (Table S1). The structural features also support that there is no π-interaction between the negative charge and the benzene ring.

Finally, it is of interest to examine the charge distribution in phenylacetylide anion because an orbital with a negative charge formed by deprotonation should be orthogonal to π-orbitals of benzene ring and the triple bond. The electrostatic potential-derived charges were computed using the CHELPG (Charges from Electrostatic Potentials using a Grid based method) scheme of Breneman and Wiberg.[25] The results are given for the anions in Table S2. The charges of the unsubstituted anions of the respective systems are illustrated in Fig. 4.

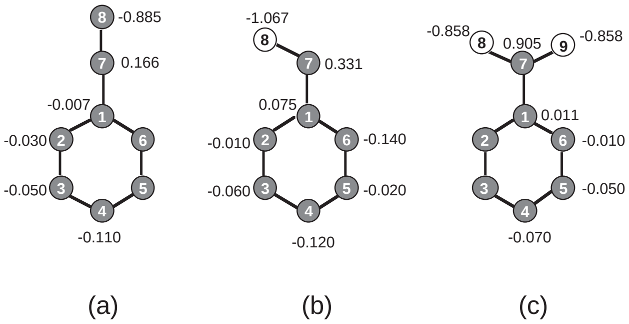

Fig. 4. Numbering of atoms (hydrogens are not shown) and the CHELPG charges of phenylacetylide (a), benzyl oxide (b), and benzoate anions (c). The charge at a hydrogen is summed to the carbon atom bonded.

The distribution of the CHELPG charges in anions indicates that most of the negative charge is localized at the terminal atoms in all systems, and that the C≡C moiety in the phenylacetylide, the CH_2O moiety in the benzyloxide, and the CO_2 moiety in the benzoate anion have ca. 70–80% of the negative charge.

In conclusion, it has been shown that the gas phase acidities of phenylacetylenes are related linearly to those of benzyl alcohols and benzoic acids with slopes of unity and that the substituent effects of all three systems are excellently correlated with $\sigma^{\rm o}_{\rm (g)}$, leading to the conclusion that there is no direct π-electron interaction between the substituent in the benzene ring and the negative charge in the phenylacetylide anion. The calculated acidities at the MP2/6-311++G**//B3LYP/6-311++G** level of theory reproduced the same substituent effects as those observed in the gas phase, and the geometrical features and charge distributions within the anions support the view that $\sigma^{\rm o}$ parameters are most appropriate for correlations in these three systems.

Experimental

Chemicals. All compounds used in this study were available from our previous study[26] and from commercial sources. Prior to use, all chemicals were purified by gas chromatography and their purities were checked by ^{1}H NMR and mass spectra in positive mode on a FT-ICR spectrometer.

Gas-Phase Acidity Measurement. The gas phase acidity measurements were performed on an Extrel FTMS 2001 Fourier transform ICR spectrometer. Most of the experimental techniques used for the measurements of the equilibrium constants of the reversible proton-transfer reactions (9) are the same as the general procedures in the literature.[27] Equations 6–9 describe the sequence of reactions which occur in a typical experiment, where AH and A_oH are the measured acid and the reference acid, respectively.

$$\mathrm{MeONO} + \mathrm{e}^- = \mathrm{MeO}^- + \mathrm{NO} \quad (6)$$
$$\mathrm{MeO}^- + \mathrm{A_oH} = \mathrm{A_o}^- + \mathrm{MeOH} \quad (7)$$
$$\mathrm{MeO}^- + \mathrm{AH} = \mathrm{A}^- + \mathrm{MeOH} \quad (8)$$
$$\mathrm{A}^- + \mathrm{A_oH} = \mathrm{A_o}^- + \mathrm{AH}. \quad (9)$$

An experiment is initiated by a 5 ms pulse of a low-energy electron beam (0.3 to 0.5 eV) through the ICR cell. The electrons are captured by methyl nitrite at a partial pressure of $1\text{–}2 \times 10^{-7}$ Torr and CH_3O^- is produced (6). The acids AH and A_oH react with CH_3O^- to yield $M - 1$ negative ions (7, 8). The partial pressure of the enols were maintained at lower than 4×10^{-7} Torr. The equilibrium constant K for reaction (9) was evaluated from the expression $K = [A^-/A_o{}^-][A_oH/AH]$. The relative abundances of ions A^- and $A_o{}^-$ were determined by the relative intensities of ICR mass spectra signals when the equilibrium was attained. For some cases, the time for the establishment of equilibrium was between 500 ms and 5 s, depending upon the pressure of neutrals. Each measurement was performed at several ratios of partial pressures and at different overall pressures. The pressures of the neutral reactants were measured by means of a Bayard-Alpert type ionization gauge with appropriate correction factors being applied to correct the gauge readings for the different ionization cross sections of the various compounds.[28] Arithmetic mean values of K were used to calculate ΔG° with an average uncertainty of ± 0.8 kJ mol^{-1} in most cases. Ion-eject experiments using the SWIFT technique[29] were also carried out to ensure that proton-transfer reactions occurred. The gas-phase acidity values for the reference compounds were taken from the literature.[16] Although the measurement of each proton transfer equilibrium was carried out at 323 K, the acidity values obtained can be regarded as the values at 298 K, because the entropy term is relatively small in proton transfer equilibria in the gas phase and because the acidities of reference compounds are compiled at 298 K.

Calculations. DFT and MP2 calculations were carried out using the Gaussian 98 program.[30] The geometries were fully optimized at the B3LYP/6-311++G** level of theory. Vibrational normal mode analyses were performed at the same level to ensure that each optimized structure was a true minimum on the potential energy surface. A single point calculation was carried out at MP2/6-311++G** using geometries calculated at the B3LYP/6-311++G** level.

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Supporting Information

Bond lengths of optimized structures for anions and neutrals (Table S1); selected CHELPG charges of anions (Table S2). This material is available free of charge on the Web at: http//www.csj.jp/journal/bcsj/.

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