Acta Chem. Scand., **17**, 2423 (1963); J. Munch-Petersen, *Bull. Soc. Chim. Fr.*, **33**, 471 (1966).

(7) The reaction of diethyl malonate with **3b** using KO-*t*-Bu as a base afforded the corresponding 1,4-adduct in an optical yield of 86%, but its absolute configuration was found to be contrary to that predicted by Scheme I. Details will be published in due course.

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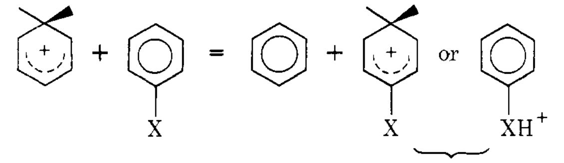
Substituent Effects on the Intrinsic Basicity of Benzene: Proton Affinities of Substituted Benzenes

Sir:

Recently there has been considerable interest in examining the intrinsic substituent effects on the basicity of benzene. The interest is justified by the fact that the protonation of benzene represents a prototype of electrophilic attack on the benzene ring and is therefore closely connected with the Hammett type linear free relationships and σ values for substituents. The intrinsic or "dilute gas phase" basicities are independent of solvent and therefore indispensible in separating true electronic effects from solvent effects of substituents.

Theoretical calculations for the energy change in the isodesmic[1] proton transfer (1) and experimental measurements by ICR of the equilibrium (1) where X = alkyl were reported recently by Hehre et al.[2] More extensive calculations including heterosubstituents were also reported later.[3] A brief discussion of the halo-substituent effects was published recently from our laboratory in connection with a general survey of compounds having proton affinities between those of water and ammonia.[4]



(1)

The present experimental results are summarized in Table I. The data are based on proton transfer equilibria measurements at 600 K, involving also a number of other bases like dimethyl ether, acetone, ethyl formate, isobutene etc., such that a complete ladder of equilibria[4] was obtained between the compounds with lowest and highest basicity. An average of three thermodynamic cycles connected each compound to the ladder. The proton affinity of aniline was obtained on basis of PA(NH_3) = 202 kcal/mol[4,5] and earlier work.[6] The present results, where overlapping with our earlier measurements,[4] were in agreement within ~0.3 kcal/mol. However, the PA values quoted in the present work are higher by ~1 kcal/mol because here we have used the new $\Delta H_f(H^+)$ = 367 kcal/mol.[7]

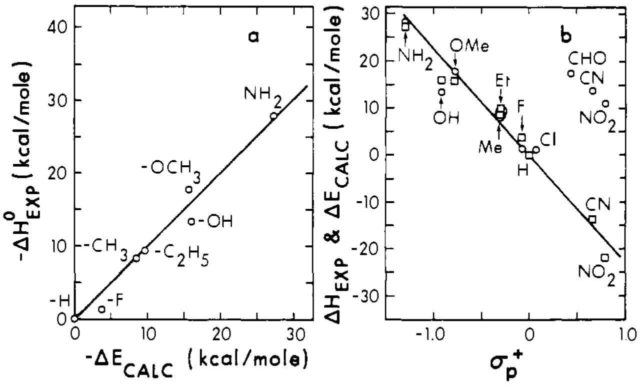


Figure 1. (a) Comparison between experimental ΔH_1 values and STO-3G calculated values for reaction 1: $C_6H_7^+ + XC_6H_5 = C_6H_6 + XC_6H_5H^+$. Straight line corresponds to 45° angle or perfect agreement. (b) Comparison between ΔH_1 ○ and ΔE_1 □ in a $\sigma_p{}^+$ plot of substituent constants. Deviations of ΔH_1 values for X = CHO, CN, NO_2 due to substituent protonation for these compounds.

The measurements were done at 600 K in order to avoid interference from the dimers B_2H^+. These dimers can become the major ions at lower temperatures if the charge in BH^+ is concentrated on a few hydrogens as is the cases NH_4+ or H_3O^+. The tendency to form dimers for ring protonated BH^+ is very much lower. This allowed us to examine the temperature dependence of K_1 for the two reactions where X = F and Cl, over a wide temperature range (25-360 °C). The linear van't Hoff plots gave in both cases $\Delta S°_1 = -3.5 \pm 0.1$ eu. The entropy change expected, because of changes of rotational symmetry numbers in these two reactions, is $\Delta S_{\text{rot.s.}} = (R \ln 1)/6 = -3.56$ eu. The closeness of the experimental entropy

Table I. Proton Affinities of Substituted Benzenes and Energy Differences for Reaction 1[a]

Substituent X	PA,[b] kcal/mol	$-\Delta G°_1(600)$[c]	σ_B/σ_{BH^+}[d]	$-T\Delta S_{\text{rot.s.}}$	$-\Delta H°$[f]	$-\Delta E$[g]	σ_{p^+}[h]
NH_2	209.3[i]	25.6[i]	1	2.1	27.7	27.2	−1.3
OMe	199.4	15.7	1	2.1	17.8	15.7	−0.778
CHO	199.1	15.4	1	2.1	17.5		0.44
CN	195.1	11.4	1	2.1	13.5	−13.8	0.66
OH	195.0	11.3	1	2.1	13.4	16.0	−0.92
NO_2	192.6	8.9	1	2.1	11.0	−22.1	0.79
Et	191.0	7.3	1	2.1	9.4	9.7	−0.295
Me	190.0	6.3	1	2.1	8.4	8.5	−0.311
H	183.7	0	6	0	0	0	0
F	182.9	−0.8	1	2.1	1.3	3.7	−0.073
Cl	182.7	−1.0	1	2.1	1.1		0.114

[a] All energy values in kcal/mol. [b] Based on $\Delta H_f(t\text{-}C_4H_9^+)$ = 169 kcal/mol (ref 5), which with new $\Delta H_f(H^+)$ = 367 kcal/mol[7] leads to PA(isobutene) = 194.2 kcal/mol, and experimental $\Delta G°(600)$ for proton transfer reactions. [c] Free energy change at 600 K for reaction 1. [d] Ratio of rotational symmetry numbers. [e] $\Delta S_{\text{rot.s.}}$ represents entropy change for reaction 1 due to changes of the rotational symmetry σ numbers. This is believed to be the major contribution to the total entropy change of reaction 1. [f] Experimental enthalpy change for reaction 1 calculated from: $\Delta G°_1(600) = \Delta H - T\Delta S_{\text{rot.s.}}$. [g] Theoretical results LCAO-MO, STO-3G obtained by Hehre[2] for reaction 1. [h] σ constants for para substituents from ref 8. $\sigma_p{}^+(NH_2) = -1.3$ from J. E. Leffler and E. Grunwald, "Rates and Equilibria in Organic Chemistry", Wiley, New York, N.Y., 1963, p 204. $\sigma_p(CHO) = 0.44$ from J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley, New York, N.Y., 1975, p 66. [i] From previous measurement in ref 6 and PA(NH_3) = 202 kcal/mol[4] based on $\Delta H_f(H^+)$ = 367 kcal/mol.[7]

change shows that for these two and probably most other substituents $\Delta S_1 \approx \Delta S_{\text{rot.s.}}$. The ΔH_1 values shown in Table I were obtained under this assumption. Also shown in Table I are the STO-3G calculated[2] energy changes ΔE_1. A comparison between these ΔH_1 and ΔE_1 changes is given in Figure 1a, while Figure 1b gives a plot of the ΔH_1 and ΔE_1 values vs. the constants $\sigma_p{}^+$ of Brown and Okamoto[8] for para substituents.

Examination of Figure 1a shows on the whole a very good agreement between the experimental ΔH_1 and the theoretical ΔE_1. In Figure 1b again a good correlation is obtained between the ΔH_1 and the substituent constants $\sigma_p{}^+$, except for nitro-, cyanobenzene, and benzaldehyde, which are way out. Evidently protonation for these three compounds occurs not on the ring but on the substituent. All these substituents have lone pairs which can accommodate the proton. More importantly they are strongly electron-withdrawing substituents which destabilize the ring protonated ion. The good agreement of the results in Figure 1a and 1b show that in all other cases ring protonation in para position to the substituent can be occurring. For the alkyl and halo substituents and even HO- and CH_3O- this is not a surprising finding; however, the possibility of ring protonation in aniline is rather unexpected. The hydroxy, methoxy, and amino group are substituents that strongly stabilize the benzenium ion; on the other hand, phenyl is electron withdrawing and thus destabilizing for substituent protonation. Thus the protonation occurs on the ring and takes advantage of the stabilizing effect of the substituent. Ring protonation in -OH and $-OCH_3$ is in agreement with an earlier investigation of deuterium exchange by Beauchamp[9] and a recent correlation of oxygen 1s core electron energies with proton affinities by Harrison.[10] On the other hand Buttrill,[11] in a recent investigation, has come to the conclusion that substituent protonation occurs for those compounds. Buttrill observed strongly bonded $XC_6H_7{}^+{\cdot}OH_2$ hydrates for X = OH and CH_3O and argued that this would happen only if there is substituent protonation. In view of the present results, Buttrill's experiments can be interpreted as showing that the site of protonation is solvent dependent. It is known from NMR experiments in solution[12] that hydrogen-bonding solvents promote substituent protonation because of the strong hydrogen bonds that can be formed. For the same reason aniline is substituent protonated in polar solvents. Probably the proton affinity for N protonation of aniline is very close to that for ring protonation.[13] A correlation similar to that by Harrison,[10] but for 1s energies of N atoms, may be expected to provide the answer.

The values for OH in Figure 1 show considerable deviation from the σ correlation. It has been pointed out previously that this is due to the hydrogen bonding of the OH group to the solvent.[1,12] The reason for the disagreement between the ΔH and ΔE results for the OH and OCH_3 substituents (Figure 1a) is not clear.

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(12) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

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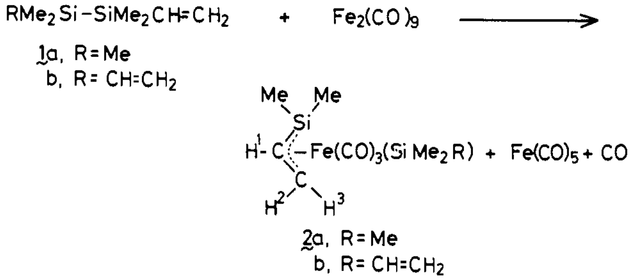
η^3-1-Silapropenyltricarbonyliron Complexes. The First Stable Compound of Doubly Bonded Silicon[1]

Sir:

It is well known that a transition metal can stabilize highly unstable molecules such as the allyl radical, cyclobutadiene, trimethylenemethane, and pentalene by forming stable complexes.[2] Although various attempts have been made also to stabilize unstable organosilicon species like silaethene[3] and "π-silaallyl"[4] by coordination with a transition metal, no success has been reported.

We report here the first preparation of η^3-1-silapropenyl complexes of iron. These complexes are the silicon analogues of π-allyl complexes and represent the first stable compounds of "doubly bonded silicon".

Enneacarbonyldiiron (200 mg, 0.55 mmol) and vinylpentamethyldisilane (**1a**, 230 mg, 1.45 mmol) were mixed with dry benzene (10 ml), and the yellow suspension was stirred at room temperature during 17 h under an argon atmosphere. A yellow-brown homogeneous solution was obtained at the end of the reaction. The solvent and volatile materials were evaporated and the residue was distilled under reduced pressure (~10^{-3} mmHg) to give a yellow-brown oil. A hexane solution of the oil was purified by preparative TLC on silica gel. After elution with hexane and evaporation, the residual oil was fractionated with a short column to give 100 mg (61.1% yield) of an analytically pure complex (**2a**), bp 45.0 °C (5×10^{-3} mmHg). The yellow complex, **2a**, was air sensitive and decomposed gradually on exposure to air, but was fairly stable thermally up to 80 °C.



The structure of the complex was determined on the basis of various spectroscopic studies to be (η^3-1,1-dimethyl-1-silapropenyl)(trimethylsilyl)tricarbonyliron as follows. The proton NMR spectrum of **1a** in carbon disulfide (Figure 1a) shows three Si-CH_3 signals at δ 0.15, 0.27, and 0.38 ppm with relative intensity of 1:3:1. These signals can be assigned to the *anti*-CH_3Si, $(CH_3)_3$Si, and *syn*-CH_3Si, respectively, in reference to the spectral data of the related π-allyliron complexes.[5] Vinyl protons of **2a** appear at higher field than the free