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Preliminary communication

CALCULATED ENERGIES FOR PROTON ABSTRACTION FROM SUBSTITUTED BENZENES, AND THEIR SIGNIFICANCE FOR BASE CLEAVAGE OF ARYLTRIMETHYLSILANES*

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Summary

The energies required for deprotonation of the substituted benzenes XC_6H_5 have been calculated by an ab initio method. The results show that substituent effects in base cleavage of $XC_6H_4SiMe_3$ compounds (and possibly those in base-catalysed hydrogen exchange in substituted benzenes) are consistent with formation of the aryl carbanion $XC_6H_4^-$ in the rate-determining step.

Studies of solvent isotope effects for cleavages of aryl—MMe_3 bonds in MeOH—MeONa have shown that for M = Sn there is proton transfer from the solvent to the aryl group ("electrophilic assistance") as it separates, while for M = Si the results are most simply interpreted as involving separation of a free aryl carbanion [1]. They do not, however, completely rule out the possibility of a small degree of electrophilic assistance even for silicon compounds, and for cleavages of $XC_6H_4SiMe_3$ compounds in H_2O—Me_2SO—KOH [2, 3] the effects of the substituents X seemed to be more compatible with such assistance [3]. To throw light on this problem, we have carried out ab initio calculation of the energy change, $E_X^- - E_X$ on going from XC_6H_5 (Energy = E_X) to $XC_6H_4^-$ (Energy = E_X^-). (The energies were derived by minimum basis set (STO-3G) ab initio calculations using the Gaussian 70 package [4] and standard geometries [5].

The results of the calculations are shown in Table 1, which includes the values of the quantity ΔE_X^-, given by $[(E_X^- - E_X) - (E_H^- - E_H)]$, which is the difference between the energy of proton abstraction from XC_6H_5 and that from benzene (X = H). The outstanding feature in the present context is the smallness of the effects of p-OMe and p-NH_2 groups on the deprotonation energy, since it

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*No reprints available.

TABLE 1

CALCULATED ENERGIES ($E_X^- - E_X$) (in a.u.) REQUIRED FOR CONVERSION OF XC_6H_5 INTO $XC_6H_4^-$

X	$E_X^- - E_X$	$-10^3\,\Delta E_X^{-\,a}$	X	$E_X^- - E_X$	$-10^3\,\Delta E_X^{-\,a}$
o-NO_2	0.776	48	H	0.824	0
m-NO_2	0.789	35	*o*-Me	0.824	0
p-NO_2	0.782	42	*m*-Me	0.825	−1
o-Cl	0.795	29	*p*-Me	0.826	−2
m-Cl	0.801	23	*o*-OMe	0.818	6
p-Cl	0.804	20	*m*-OMe	0.819	5
o-F	0.811	13	*p*-OMe	0.826	−2
m-F	0.814	10	*o*-NH_2	0.828	−4
p-F	0.820	4	*m*-NH_2	0.827	−3
			p-NH_2	0.838	−14

[a] Value of $(E_X^- - E_X) - (E_H^- - E_H)$, where E_H refers to C_6H_6.

was previously argued that these groups, which release electrons strongly by resonance effects, would be expected to cause large destabilization of the anions. There is in fact, a good linear correlation (corr. coeff., 0.978, for 13 points) between the values of ΔE_X^- (the values for *m*- and *p*-NH_2 being assumed to be approximately applicable to the corresponding NMe_2 groups) and those of log k_{rel} (k_{rel} is the rate constant for $XC_6H_4SiMe_3$ relative to that for $C_6H_5SiMe_3$) for cleavage of $XC_6H_4SiMe_3$ compounds in 9/1 H_2O—Me_2SO, for which the most extensive set of data is available [2]. We conclude that the substituent effects are consistent with separation of the free aryl anions, and that there is now no basis on which to doubt that the cleavages of arylsilicon compounds in MeOH—MeONa do, indeed, involve free carbanions.

The values of ΔE_X^- do not give a linear correlation with the very rough values of log k_{rel} for hydrogen-exchange of XC_6H_5 compounds in liquid ammonia [6], and this is consistent with a mechanism involving electrophilic assistance [3], but the uncertainties in the rate data preclude a firm decision; it is noteworthy, however, that the outstanding feature, viz. the smallness of the deactivating effects of *p*-NMe_2 and *p*-OMe groups relative to those of other substituents (cf. ref. 3), is now compatible with the formation of free carbanions. The substituent effects in cleavages of $XC_6H_4SnMe_3$ compounds in MeOH—MeONa [7], in which the *p*-OMe and *p*-NMe_2 groups raise the reactivity, are fully consistent with the mechanism involving electrophilic assistance, though with considerable aryl anion character in the rate-determining transition state [3].

A full analysis of the significance of the calculations will be published later.

References

1 C. Eaborn and G. Seconi, J. Chem. Soc. Perkin II, (1976) 925.
2 J. Cretney and G.J. Wright, J. Organometal. Chem., 28 (1971) 49.
3 A.R. Bassindale, C. Eaborn, R. Taylor, A.R. Thompson, J. Cretney and G.J. Wright, J. Chem. Soc. B, (1971) 1155.
4 W.J. Hehre, W.A. Latham, R. Ditchfield, M.D. Newton and J.A. Pople, Program 236, Quantum Chemistry Program Exchange, Indiana Univ., 1971.
5 J.A. Pople and M. Gordon, J. Amer. Chem. Soc., 89 (1967) 4253.
6 A.I. Shatenshtein, Tetrahedron, 18 (1962) 95; G.E. Hall, R. Piccolini and J.D. Roberts, J. Amer. Chem. Soc., 77 (1953) 4540; G.E. Hall, E.M. Libby and E.L. James, J. Org. Chem., 28 (1963) 311; A. Streitwieser, R.A. Caldwell, R.G. Lawler and G.R. Ziegler, J. Amer. Chem. Soc., 87 (1965) 5399.
7 C. Eaborn, H.L. Hornfeld and D.R.M. Walton, J. Chem. Soc. B, (1967) 1036.