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Electron Affinities of Benzaldehydes. Substituent Effects on Stabilities of Aromatic Radical Anions

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Abstract: Relative electron affinities have been determined for a series of benzaldehydes by measurement of electron transfer equilibria in the gas phase with a pulsed ICR spectrometer. It has been shown that the substituent effect on the electron affinity of benzaldehyde has been described in terms of the LArSR Eq. 1 with an r of 1.11 greater than that for electron affinities of nitrobenzenes.

One of the fundamental properties of an organic molecule is the electron affinity that is the lowest energy required to remove an electron of a negative ion. In recent years relative electron affinities have been determined

$$A^{-} \rightleftharpoons A + e^{-} \qquad (1)$$

for various compounds based on measurements of gas phase electron-transfer equilibria using a pulsed high pressure-source mass spectrometer (HPMS) and a pulsed ion cyclotron resonance (ICR) spectrometer.1) Much attention is being donated to the substituent effect on electron affinities of aromatic compounds since the finding of a striking similarity between the substituent effects on the electron affinities of nitrobenzenes and the acidities of phenols and anilines by McIver and Fukuda.2, 3) More recently Kebarle and coworkers have analyzed the substituent effects on electron affinities of nitrobenzene,4, 5) benzonitrile,6) pentafluorobenzene,7) and benzene series based on limited data sets in some cases, and suggested that the more stable radical anion has the lower response to the change of substituent resonance effect.7) This trend is qualitatively consistent with previous results of the LArSR analysis8-10) for the stabilities of benzylic carbocations in the gas phase.11-15) That is,

$$\delta\Delta G^{\circ} = \rho(\sigma^{\circ} + r^{\pm}\Delta\bar{\sigma}_{R}^{\pm}) \qquad (2)$$

the LArSR analysis for the stabilities of benzylic carbocations revealed that the resonance demand (r) increases linearly with the decrease in stability of the unsubstituted member of each series while ρ value remains constant within a series of benzylic carbocations. It is therefore of particular interest to examine applicability of the LArSR analysis to the substituent effect on the electron affinities of aromatic compounds. This would also help our understanding of properties of the π*-type singly occupied molecular orbital (SOMO) of radical anions and would provide a new insight into the factors responsible for the similarity with the acidity substituent effects related to the energy of the HOMO of the molecule. In this study the substituent effects on electron affinity have been examined for benzaldehyde and benzonitrile series as a system of which radical anion is less stable than the corresponding nitrobenzene.

The equilibrium constants for electron-transfer reaction (3), K_3, involving benzaldehydes and a series of appropriate reference compounds were measured on a pulsed ICR spectrometer built in our laboratory.16) An experiment is initiated by a low energy (ca. < 1 eV) electron beam pulse through the ICR cell. The electron transfer equilibrium is achieved within 1s of initiation of the reaction, and the equilibrium constant K_3 and free energy change $\Delta G^o{}_3$ can be calculated from relative abundances of two negative ions and the partial pressures of the neutral molecules. Since electron attachment free energy, $\Delta G^o{}_a$, corresponding to the free energy for

$$A^- + B \rightleftharpoons A + B^- \qquad (3)$$

$$K_3 = \frac{[B^-][A]}{[A^-][B]} \qquad (4) \qquad\qquad \Delta G^o{}_3 = -RT \ln K_3 \qquad (5)$$

electron capture is available from literature for the reference compounds, $\Delta G^o{}_a$ could be evaluated for the *m, p*-substituted benzaldehydes from the relative $\Delta G^o{}_3$ values. Several electron affinity values have been added to the benzonitrile and nitrobenzene series for a comparison.

Table 1. Relative Electron Affinities

	ΔEA/kcal mol^{-1} a)		
Subst.	CHO$^{b)}$	CN$^{c)}$	NO$_2$$^{d)}$
p-NO$_2$	28.1	33.6	21.5
p-CHO	19.8	22.6	14.9
p-CN	18.2	20.3	15.9
p-CF$_3$	12.7	13.1	11.0
p-CO$_2$Me	14.6	17.1$^{b)}$	10.7$^{b)}$
m-NO$_2$	21.8	29.3	14.1
m-CN	13.3	15.5	12.0
m-CHO	13.4	17.7	8.9
m-CF$_3$	9.8	10.0	8.8
3,5-(CF$_3$)$_2$	19.4	20.8	17.4$^{e)}$
3,5-Cl$_2$	13.8	13.9$^{b)}$	12.4$^{b)}$
m-Cl	6.4	—	6.0
p-Cl	6.2	—	5.4
H	(9.9)$^{f,g)}$	(5.5)$^{f,g)}$	(22.8)$^{f)}$

a) $\delta\Delta G^o{}_a$ at 343 K, 1 cal = 4.184 J. b) This work. c) Ref. 6. d) Ref. 5. e) Ref. 1. f) Absolute electron affinity values. g) Ref. 17.

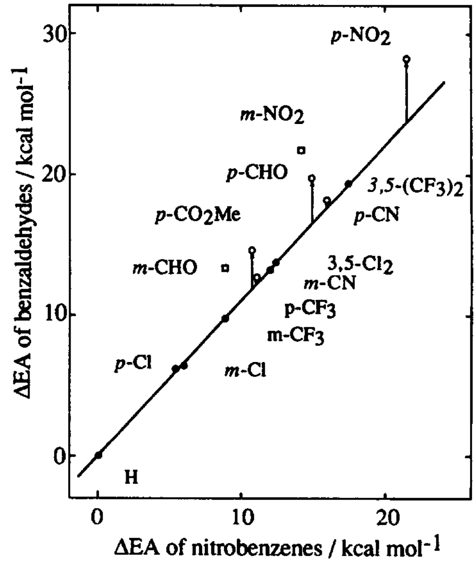

Fig. 1. Plots of ΔEAs of benzaldehydes vs. the corresponding nitrobenzenes.

In Fig. 1 are plotted relative electron affinities of benzaldehydes against the corresponding nitrobenzenes. There is evidently no excellent linear relationship as a whole. When the substituents are limited for meta substituents except *m*-NO$_2$ and *m*-CHO, one can find an excellent linear relationship with a slope of 1.1. With respect to this meta line strongly electron-withdrawing para substituents show systematic deviations, i.e., the stronger π-acceptor gives the greater deviation. Such deviation patterns suggest exalted resonance effects of π-acceptors in benzaldehyde radical anions compared with that in the nitrobenzene radical anions. Similar situation has been observed for electron affinities of benzonitrile series (Fig. 2) though deviations of para π-acceptors are somewhat larger. These trends are consistent with the concept of varying resonance demand introduced into the LArSR Eq. 2. In fact, the LArSR Eq. 2 could be applied successfully to electron affinities of benzaldehyde, benzonitrile, and nitrobenzene series with standard substituent constant values, σ^o and $\Delta\bar{\sigma}_R$, for most of substituents except *p*-NO$_2$ group.[18] Although a new substituent constant set may be required for subsitituent effect analysis of an odd electron system like electron affinities, the high correlation coefficient of the present results suggest that the standard substituent parameters derived from an even electron system like acidities of phenols in solution are useful still as a first approximation. The r⁻ value is found to increase significantly from 0.62 to 1.29 as the anion series changes from nitrobenzene radical anion to the corresponding benzonitrile, being consistent with graphical analysis noted above. This indicates that the resonance effect contribution of π-acceptors to the stability of radical anion varies essentially with the system. Furthermore, the change of the r value seems to be related inversely to the electron affinity of unsubstituted member of each series. Indeed, we can find a good linear relationship between the r values and electron affinities of unsubstituted member as shown in Fig. 3. This relationship is reconciled with previous observations for substituent effects on stabilities of benzylic carbocations, supporting the conclusion that the resonance demand is a function of the intrinsic stability of an ion.[14, 15] The present result suggests further that the π*-type electron in the SOMO of the radical anion is delocalized onto the π-acceptor para-substituents in a similar mechanism as that of even electron anions like phenoxides and anilides. The variation of the r value with the system may be easily rationalized. The electron affinity increase of the unsubstituted member of each series will lower progressively electron density in the π*-type SOMO extending over the benzene ring of the negative ion, i. e., much of electron is located on the substituent. This seems to be consistent with theoretical calculations for mono-substituted benzene radical

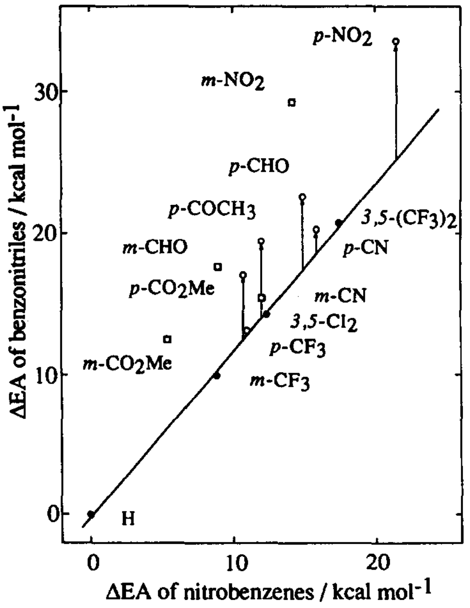

Fig. 2. Plots of ΔEAs pf benzonitriles vs. the corresponding nitrobenzenes

Table 2. LArSR Correlation Results for Electron Affinities of Aromatic Compounds

Series	ρ	r⁻	R[a)]	EA[b)]
Nitrobenzene	18.1	0.62	0.994	22.8
Benzaldehyde	18.8	1.11	0.998	9.9
Benzonitrile	21.0	1.29	0.996	5.5

a) Correlation coefficient. b) Electron affinity of the unsubstituted member of each series in kcal mol^{-1}.

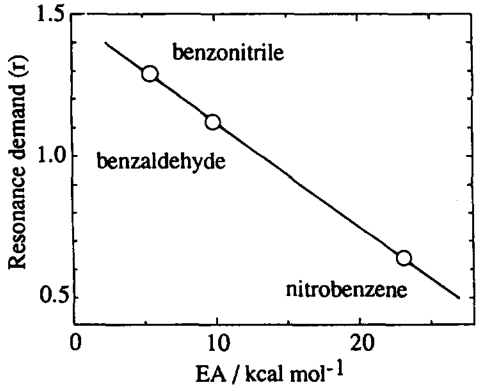

Fig. 3. Relationship between the r value and EA of the unsubstituted member of each series.

anions that strongly electron-withdrawing substituents cause the decrease of π–electron density in position para to the substituent, e. g., π-electron density on the ring carbon para to NO_2 (1.201 e) is lower than that for CHO (1.236 e) and CN (1.250 e).[19] Hence, in the lower electron affinity compounds like benzonitrile and benzaldehyde the electron-withdrawing para substituent X will have a strong π-interaction with the aromatic SOMO electron. This would cause the increase of the r value.

It is of interest to note that the effects of the *m*-nitro and *m*-formyl groups are remarkably large in the benzaldehyde radical anion compared with those in the nitrobenzene radical anion as seen in Fig. 1. In the benzaldehyde radical anion NO_2 or CHO introduction leads to a large shift of SOMO density to the substituent X because NO_2 and CHO have a high electron affinity. On the contrary, when NO_2 or CHO is introduced in position 3 of nitrobenzene radical anion, the SOMO density shift to it will be considerably smaller since the substituent does not overpower the equally strong initial NO_2. Consequently, the effects of *m*-NO_2 and m-CHO on the electron affinity of benzaldehyde appear to be out of a range of perturbation termed as substituent effect analysis. This may account for deviations of *m*-NO_2, *m*-CHO, and *m*-CO_2Me observed in benzonitrile series. On the other hand, when these substituents are introduced in position 4, the substituent X will cause the reorganization of the distribution of an added electron in the radical anion because π-electron acceptor substituents like CHO, CN, and NO_2 lead to preference for the $^2B_{1u}$ π^* orbital as the SOMO that has high electron density in position para to the substituent.[19] This is consistent with experimental observation that the LArSR correlation can describe well the effects of these strong π-acceptor para substituents as well as other π-acceptors.

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