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Substituent Effect on Electron Affinity of 2,6-Dimethylnitrobenzene

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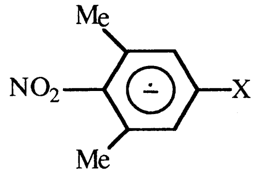
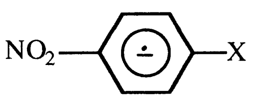
Electron affinities have been determined for a series of 2,6-dimethyl-4-substituted nitrobenzenes, where the nitro group is twisted out of the coplanarity with the benzene ring, by measurement of electron transfer equilibria in the gas phase with a pulsed ICR spectrometer. The substituent effect of this system has been found to be in agreement with that of the planar nitrobenzene system.

Since the first measurement of the electron-transfer equilibria in gas-phase by McIver and Fukuda,1-3) a number of electron affinity (EA) values have been determined by the equilibrium method with a pulsed high pressure mass spectrometer (HPMS),4-9) a pulsed ion cyclotron resonance spectrometer (ICR),2, 3, 10, 11) and flowing afterglow apparatus.12) These data provided a valuable basis of structural effect on the thermodynamic properties of a radical anion which is one of the most important intermediates of organic reactions.9) The substituent effect on EA of nitrobenzene has been studied first by McIver and Fukuda,3, 11) and an excellent linear correlation between the electron affinities of nitrobenzenes and the relative gas-phase acidities of phenols and anilines was observed. Kebarle and coworkers also analyzed this substituent effect more in detail by the aid of the Taft DSP analysis and frontier orbital theory using a comprehensive data set.8, 9) A striking similarity between the substituent effects on the electron affinities of nitrobenzenes and the acidities of phenols and anilines suggested that a similar mechanism for charge delocalization exists in the nitrobenzene, phenoxide, and anilide negative ions. This may be consistent with theoretical calculations that 0.54 of an electronic charge are delocalized to the benzene ring in the nitrobenzene radical anion and that larger densities develop in positions ortho and para to the nitro group in a manner similar to that for phenoxide and anilide.13) Since the extra electron in the nitrobenzene is in a π^*-type orbital which extends over the nitro group and the benzene ring, the electron affinities are generally related to the energy of the LUMO of the molecule. On the other hand the acidities of phenols and anilines are related to the energy of the HOMO of the molecule. Considering such differences, the similarity of the substituent effect between electron affinities of nitrobenzenes and acidities of phenols may be surprising. In this study, we have examined the substituent effect on the electron affinity of 2,6-dimethylnitrobenzene where the common nitro group is forced out of the plane of the benzene ring owing to steric hindrance.14) Since much of the electronic charge in this radical anion must be located on the nitro group, the charge in position para to the nitro group is expected to become smaller than that in the planar nitrobenzene radical anion.14, 15) This would result in the reduced π-interaction between the substituent X and the benzene ring. Examination of the substituent effect on electron affinity of 2,6-dimethylnitrobenzene may therefore provide an important clue to uncover the factors governing the substituent effect on EA of nitrobenzene.





The equilibrium constants for electron-transfer reaction (1), K_1, involving 2,6-dimethyl-4-substituted nitrobenzenes and a series of appropriate reference compounds were measured on a pulsed ICR spectrometer built in our laboratory. 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_1 and free energy changes ΔG_1° can be calculated from relative abundances of two negative ions and

$$A^- + B \rightleftharpoons A + B^- \qquad (1)$$

$$K_1 = \frac{[B^-][A]}{[A^-][B]} \quad (2) \qquad \Delta G_1^\circ = -RT \ln K_1 \quad (3)$$

the partial pressures of the neutral molecules.$^{11, 16)}$ Since electron attachment free energy, ΔG_a°, corresponding to the free energy for electron capture is available from literature for the reference compounds, ΔG_a° could be evaluated for the 2,6-dimethyl-4-substituted nitrobenzenes from the relative ΔG_1° values. Similarly ΔG_a° values have been determined for several planar nitrobenzenes under the same conditions for a comparison. Results are summarized in Table 1 together with the corresponding values of p-substituted nitro-benzenes determined by Kebarle and coworkers (HPMS) and by McIver and Fukuda (ICR). Electron affinity values of nitrobenzenes determined in this study are in good agreement with those measured by the HPMS technique. This allows a

Table 1. Electron Affinities of 2,6-Dimethyl-4-substituted Nitrobenzenes and the Corresponding Values of p-Substituted Nitrobenzenes

	ΔEA/kcal mol^{-1} a)			
	2,6-Dimethylnitrobenzene	Nitrobenzene		
Subst.		This work	McIver$^{b)}$	Kebarle$^{c)}$
	343 K	343 K	357 K	423 K
p-NO_2	20.5	21.5	21.2	21.5
p-CN	15.2	16.2		15.9
p-CHO	14.3	14.9		14.9
p-$COCH_3$	12.4	12.6		12.0
p-CO_2CH_3	9.9	10.7		
p-Cl	5.4	5.6	4.7	5.4
p-F	2.2	2.1	1.7	2.2
p-Me	-1.6	-1.3	-1.4	-1.6
p-OMe	-2.5	-2.7		-2.5
H	0.0 (17.4)$^{d)}$	0.0 (23.1)$^{d)}$	0.0 (23.1)$^{d)}$	0.0 (22.8)$^{d)}$

a) $\delta\Delta G_a^\circ$, electron attachment free energy relative to respective unsubstituted derivatives, 1 cal = 4.184 J. b) Ref. 3. c) Ref. 6. d) Absolute electron affinities obtained by anchoring to literature value $EA(SO_2)$=26.1 kcal mol^{-1}, Ref. 8.

comparison of relative electron affinity values without a consideration of experimental conditions employed for their determinations.

The EA value of 2,6-dimethylnitrobenzene reveals that its radical anion is 5.7 kcal mol^{-1} less stable than the corresponding nitrobenzene. This destabilization would be attributed mostly to steric inhibition of the π-interaction between the nitro group and the benzene ring in addition to electronic effect of two o-methyl groups. At first glance the magnitude of the destabilization is found to be quite small compared with an overall effect of the nitro group on the electron affinity of benzene evaluated to be 49 kcal mol^{-1},[17)] indicating that the π-interaction between the nitro group and the benzene ring is relatively less important to determine electron affinity of nitrobenzene. The extent of stabilization arising from charge-delocalization into the benzene ring may be approximated by the difference in stability of radical anion between nitrobenzene and nitroalkane where the added electron is located entirely on the nitro group.[15)] Using EA of nitromethane as a reference nitroalkane,[8)] the charge-delocalization energy of 10.9 kcal mol^{-1} is obtained for the nitrobenzene radical anion. The loss of 5.7 kcal mol^{-1} observed for EA of 2,6-dimethylnitrobenzene relative to nitrobenzene seems to be reasonable as the decrease in π-interaction between the nitro group and the benzene ring caused by di-o-methyl substitution because a similar decrease in resonance effect of the nitro group is observed for the gas phase acidity of 3,5-dimethyl-4-nitrophenol.[18)] Hence it is concluded that the nitro group in the 2,6-dimethylnitrobenzene radical anion must be forced out of the plane of the benzene ring. This is consistent with the results of ESR and polarography studies.[15, 19)]

Electron-withdrawing substituents like NO_2, CHO, CN, $COCH_3$, and CO_2CH_3 lead to large increase of electron affinity, being in complete agreement with the corresponding planar system. In Fig. 1 are plotted relative electron affinities of 2,6-dimethyl-4-substituted nitrobenzenes against those of planar nitrobenzenes. There is

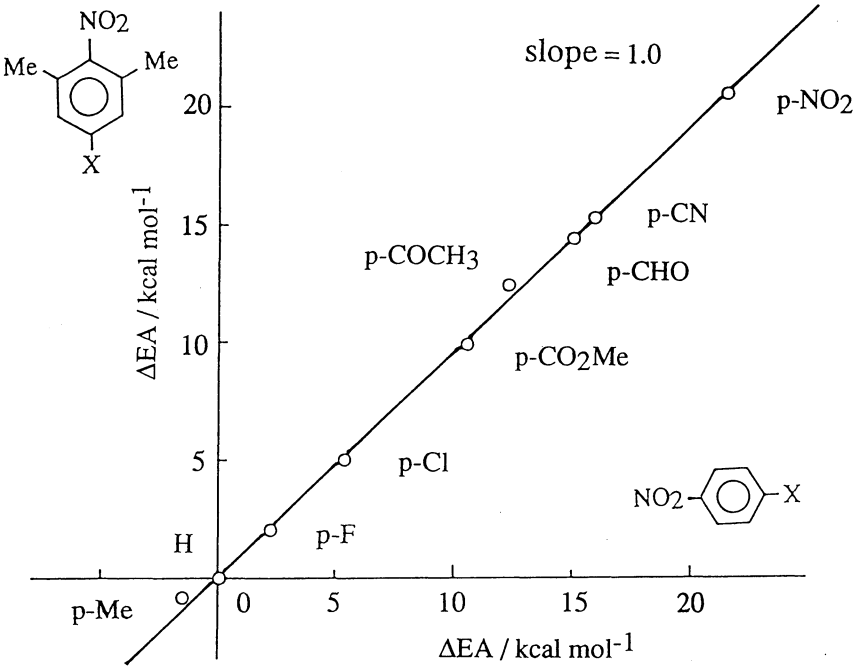


Fig. 1. Relationship between relative electron affinities of 2,6-dimethylnitrobenzenes and the corresponding values of planar nitrobenzenes.

evidently an excellent linear relationship with a slope of unity, indicating that the π-interaction between the substituent X and the benzene ring is identical with that in the planar nitrobenzene radical anion. The identity of the substituent effect in both systems leads us to the conclusion that the coplanarity of the nitro group with the benzene ring is less important to determine the substituent effect on the stability of the nitrobenzene radical anion. This may not be a surprising result because the effect of twisting of the nitro group on the electron affinity of nitrobenzene is essentially small as mentioned above. In connection with this result it should be noted that the resonance effect contribution of the substituent X to the stability of the twisted benzylic carbocation, e.g., α-t-butyl-α-methylbenzyl cation, is reduced appreciably compared with that to the corresponding planar carbocation, i.e., α-cumyl cation.[20, 21) Furthermore, the effect of the charge-delocalization to the benzene ring in the nitrobenzene radical anion, 10.9 kcal mol^{-1}, is significantly smaller than that in phenoxide, 28.0 kcal mol^{-1} given by the difference in gas phase acidity between methanol and phenol. No effect of twisting out of the nitro group on the substituent effect on EA of nitrobenzene appears to reflect characteristic nature of a singly occupied π-type orbital of nitrobenzene radical anions. In conclusion, we infer from present results that the similarity between substituent effects of electron affinities of nitrobenzenes and gas phase acidities of phenols is incidental and that there is essential difference in substituent effect behavior between an odd electron anion and an even electron anion like phenoxide. Further studies on the substituent effects on stabilities of other aromatic radical anions are in progress to explore intrinsic properties of radical anions.

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