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Solvation of Alkylbenzenes Studied by Photoelectron Emission Spectroscopy of Organic Solutions

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The external ionization potentials for alkylbenzenes in acetonitrile and nitrobenzene have been measured by photoelectron emission spectroscopy to determine electronic polarization energies and reorganization energies. The polarization energy is used to discuss the solvation structure of alkylbenzene. The solvation behavior of alkylbenzene is found to be different from that of butylamine, previously reported. We have obtained the evidence of the approach of solvent molecules to the plane of benzene ring.

The radii of solvation sphere for butylamines in acetonitrile have been determined by using photoelectron emission (PEE) technique.[1] Though their molecular shapes are not spherical, their radii correlate excellently with the molecular sizes estimated from their densities. In the present study, PEE spectra are obtained for acetonitrile and nitrobenzene solutions of several alkylbenzenes including highly symmetrical hexamethylbenzene and *o*-, *m*-, and *p*-xylene to investigate the effect of solute–solvent interaction on the size of solvation sphere.

The linear correlation has been reported by Kochi et al.[2] between ionization potential in vacuum (I_p) and oxidation potential in solution (E_{ox}) for alkylbenzene. External ionization potential (E_t) determined from PEE spectra can be combined with I_p and E_{ox} to discuss solvation structure and mechanism. The E_t value is related to I_p or the standard oxidation potential (E°_{ox}) as follows,[1,3]

$$P_+ = I_p - E_t, \tag{1}$$

$$\Delta G_r = E_t - E^\circ_{ox} - \Delta G_H, \tag{2}$$

where P_+ is the polarization energy of the solvent molecules, ΔG_r is the reorganization energy, and ΔG_H is the potential of vacuum level referred to NHE, which is estimated to be 4.5 eV.[4,5]

The polarization of solvent molecule is induced by the positive charge of photoionized solute molecule and it depends on the number of solvating molecules and their geometrical arrangement. The P_+ is related to an effective solvation radius[1] (r_{P_+}) through Born type equation,

$$P_+ = e^2(1 - 1/\varepsilon_{op})/2r_{P_+}, \tag{3}$$

where e is the charge of an electron, and ε_{op} is the optical dielectric constant of the solvent. Thus the PEE technique is expected to provide us a new parameter, the effective solvation radius, which should be used to investigate solute–solvent interaction.

The ΔG_r contains the energy caused by the change in orientation of surrounding solvent molecules (R_{out}) which is closely related to the solvation radius, and the relaxation energy of the produced cation molecule (R_{in}).

Experimental

Materials. The alkylbenzenes were purified by distillation or recrystallization. Purities of the samples were certified to be >98% by HPLC. Acetonitrile of spectra-grade was fractionated from P_2O_5 after stirring overnight. Nitrobenzene was of reagent-grade and was dried over $CaCl_2$, decanted, and distilled under reduced pressure. Tetrabutylammonium perchlorate was of special-grade (Nakarai Chemicals Co.) and used as purchased.

Photoelectron Emission Spectra. The external ionization potentials for alkylbenzenes were measured as photoionization threshold energy (E_t) by PEE technique which has been reported.[1] Sample solutions were prepared just before measurement. PEE spectra were taken at −30 °C with 0.1 mol dm^{-3} concentration for benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene and ethylbenzene in acetonitrile. The conditions for other samples were; +1 °C, 0.025 mol dm^{-3} for hexamethylbenzene and hexaethylbenzene in acetonitrile; room temperature, 0.1 mol dm^{-3} for all samples in nitrobenzene. PEE spectra in acetonitrile were also obtained at −15 °C and +1 °C. No dependence of E_t value on temperature was detected.

Water contents in acetonitrile and nitrobenzene used in this study were measured by Karl Fischer titration analysis and the contents were 3—15×10^{-3} mol dm^{-3}. It was found, however, that water in the solvents does not affect PEE spectra at all.

Cyclic Voltammetry. Cyclic voltammograms (CV) were obtained for 5×10^{-3} mol dm^{-3} of *o*-, *m*-, and *p*-xylene, mesitylene, hexamethylbenzene, and hexaethylbenzene in nitrobenzene containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate at room temperature in air-tight cell under nitrogen atmosphere. The scan rate was 8.42 V s^{-1} for all the samples. The working electrode was a 0.1 mm-diameter platinum disk electrode embedded in glass. The counter electrode was a platinum spiral wire. The reference electrode was Ag/$AgNO_3$ (0.1 mol dm^{-3}) in acetonitrile, separated from sample solution by a cracked glass. The electrode was calibrated relative to ferrocene/ferrocenium standard after every measurement and the potential was converted into NHE value by adding 0.400 V.[6]

Table 1. Photoionization Energies of Substituted Benzenes in the Gas Phase (I_p) and in the Solvents (E_t) (NB=Nitrobenzene, AN=Acetonitrile), the Oxidation Potential (E^p_{ox}), the Polarization Energies (P_+), the Reorganization Energies (ΔG_r), the Effective Solvation Radii (r_{P_+}), and the Radii of the Solute Molecules (r_d)

Solute	I_p/eV	E_t/eV		E^p_{ox}/V		P_+/eV		ΔG_r/eV		r_{P_+}/Å		r_d/Å
		NB	AN	NB	AN	NB	AN	NB	AN	NB	AN	
Benzene	9.24		8.02		2.86		1.22		0.66		2.78	2.64
Toluene	8.82	7.77	7.87		2.49	1.05	0.95		0.88	4.02	3.57	2.80
o-Xylene	8.56	7.67	7.70	2.07	2.40	0.89	0.86	1.10	0.80	4.75	3.94	2.93
m-Xylene	8.56	7.69	7.67	2.13	2.35	0.87	0.89	1.06	0.82	4.86	3.81	2.94
p-Xylene	8.44	7.64	7.56	2.07		0.80	0.88	1.07		5.28	3.85	2.95
Mesitylene	8.42	7.60	7.60	2.06	2.26	0.82	0.82	1.06	0.84	5.15	4.13	3.07
Hexamethylbenzene	7.85	7.13	7.12	1.60	1.82	0.72	0.73	1.03	0.80	5.87	4.53	3.16
Ethylbenzene	8.77	7.70	7.81		2.51	1.07	0.96		0.80	3.95	3.53	2.94
Hexaethylbenzene	7.71	7.02	7.00	1.73	1.95	0.69	0.71	0.79	0.55	6.12	4.66	3.95

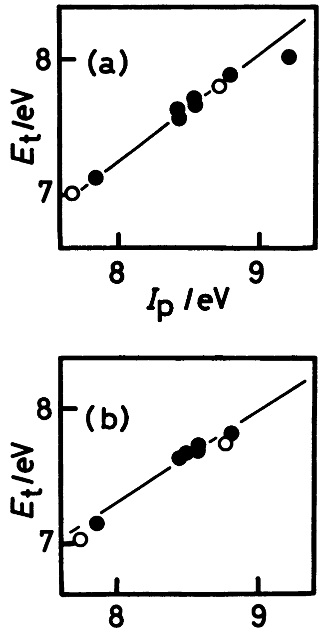

Fig. 1. The relationship between the ionization potentials in gas phase (I_p) and the external ionization potentials (E_t) in acetonitrile (a) and nitrobenzene (b). Closed circles are for methyl-substituted and open circles for ethyl-substituted benzenes.

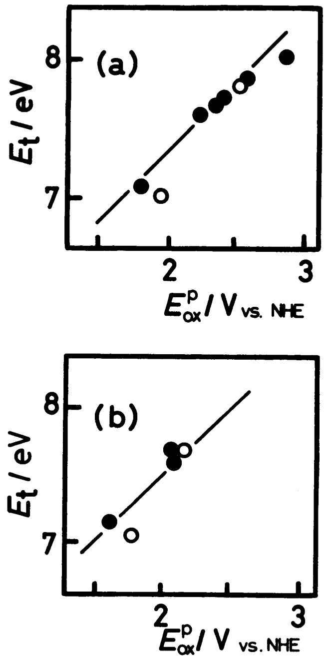

Fig. 2. The relationship between the anodic peak potentials (E^p_{ox}) and the external ionization potentials (E_t) in acetonitrile (a) and nitrobenzene (b). Closed circles represent methyl-substituted and open circles ethyl-substituted benzenes.

Results and Discussion

Correlations between E_t vs. I_p and E_t vs. E_{ox}. The E_t values obtained for alkylbenzenes are collected in Table 1, which includes I_p and anodic peak potentials of CV (E^p_{ox}). The values of I_p and E^p_{ox} in acetonitrile are taken from the work done by Kochi et al.[2] Figure 1 shows the correlation between E_t and I_p both in acetonitrile and nitrobenzene. The plot of E_t vs. I_p (except for benzene in acetonitrile) gives linear correlation as follows,

$$E_t = 0.78 \times I_p + 1.01\ \text{eV (in acetonitrile)}, \tag{4}$$

$$E_t = 0.69 \times I_p + 1.74\ \text{eV (in nitrobenzene)}. \tag{5}$$

The smaller values of the slopes than unity indicate that the polarization energy is smaller for alkylbenzene having smaller I_p value or for larger benzene in size. The linear correlation also exists between E_t and E^p_{ox} as shown in Fig. 2 and the slopes are almost unity.

$$E_t = 0.89 \times E^p_{ox} + 5.56\ \text{eV (in acetonitrile)}, \tag{6}$$

$$E_t = 1.04 \times E^p_{ox} + 5.17\ \text{eV (in nitrobenzene)}. \tag{7}$$

Polarization Energy, P_+. The polarization energy P_+ determined from the difference ($I_p - E_t$) gives us the information about the size of solvation sphere around the photoionized cation radical molecule. The solvation structure of the cation molecule is exactly the same as that of the original neutral molecule, because the photoionization process is subjected to the Franck–Condon transition.

Figures 3 and 4 show the correlation between P_+ and the number n of alkyl groups introduced to a benzene molecule. Both in acetonitrile and nitrobenzene, P_+ decreases with n, which should be the effect of the alkyl groups working as insulator locating between the positive charge on benzene ring and solvent molecules.

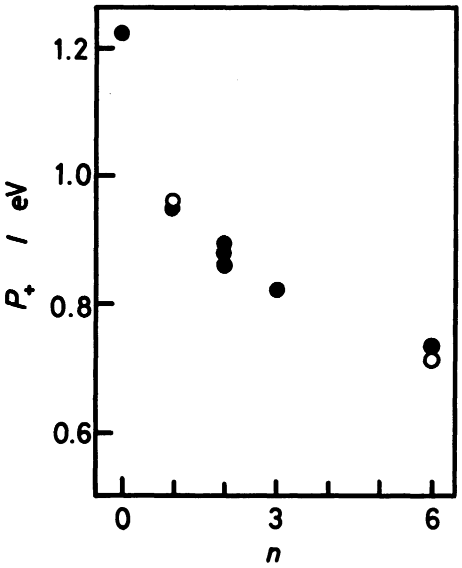

Fig. 3. The relationship between the polarization energies (P_+) and the number n of substituents introduced to benzene in acetonitrile.

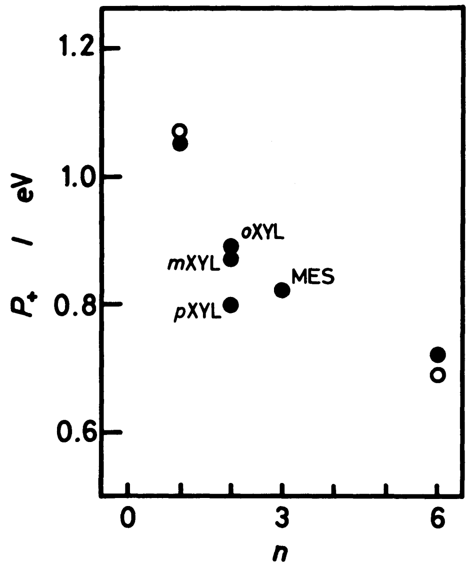

Fig. 4. The correlation of polarization energies (P_+) and the number n of substituents introduced to benzene in nitrobenzene. Closed circles are for methyl-substituted and open circles for ethyl-substituted benzenes. (*o*, *m*, *p*XYL: *o*-, *m*-, *p*-xylene, MES: mesitylene).

Symmetry of the sample molecule is distinguished by nitrobenzene solvent. Among the three dimethylbenzenes, *p*-xylene has the smallest P_+ value, and the value is even smaller than that for mesitylene. This is not the case in acetonitrile. This peculiar effect of the solvent should be related to the size, shape or dipole moment of the solvent molecule.

The change in substituent, methyl or ethyl group, causes no change in P_+ in both solvents. This will be discussed in the next section considering the effective solvation radius.

The Effective Solvation Radius, r_{P_+}. The effective solvation radius (r_{P_+}) calculated from P_+ value using Eq. 3 is compared with the radius (r_d) evaluated from the density (d) of pure substance,

$$r_d = 0.5 \times (M/dN_A)^{1/3}, \tag{8}$$

where M is the molecular weight and N_A Avogadro's constant, and the result is shown in Fig. 5. The solid line in the figure indicates the position where both of r

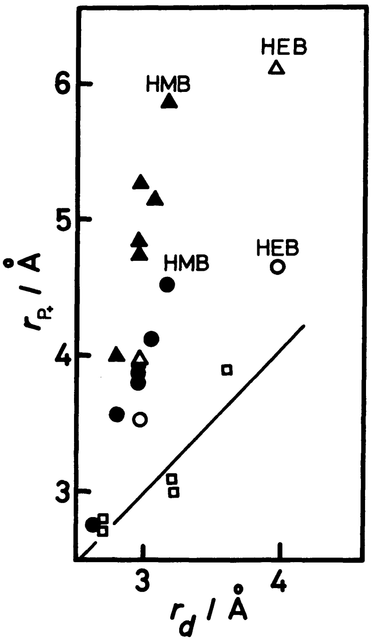

Fig. 5. The relationship between the radii calculated from the densities of the pure solutes (r_d) and the effective solvation radii calculated from the polarization energies (r_{P_+}). Closed circles are for methyl-, open circles for ethyl-substituted benzenes in acetonitrile, closed triangles are for methyl-, open triangles for ethyl-substituted benzenes in nitrobenzene. The data for butylamines are also included in this figure as open tetragons (Ref. 7). The solid line indicates the position of $r_{P_+}=r_d$.

values are the same. This figure includes the results for butylamines in acetonitrile which is previously reported.[7] While the points for amines come to the solid line excellently, the values of r_{P_+} for aromatic hydrocarbons are larger than r_d for all the samples except for benzene in acetonitrile. The experimental fact pointed out in the previous section that the substitution of methyl groups on the benzene molecule with ethyl groups does not affect the P_+ energy contradicts the prediction derived from Eq. 3. Though the value of r_d for hexaethylbenzene is significantly larger than that for hexamethylbenzene, their values of r_{P_+} are almost the same. Since the r_{P_+} is considered to be the distance of the nearest solvent molecules from the charge of the cation which locates at benzene ring,[8] the solvation structure for hexaethylbenzene can be considered to be the same as that for hexamethylbenzene. It means that the solvent molecules around hexaethylbenzene and hexamethylbenzene must locate above and beneath the benzene-ring plane of the sample molecule. If the nearest solvent molecules were in the benzene-ring plane beyond the alkyl groups, the change in length of the alkyl group should affect r_{P_+} and these two samples should have quite different r_{P_+} values.

The same trend is observed for the cases of toluene, ethylbenzene in both solvents.

Reorganization Energy, ΔG_r. The difference between E_t and the standard oxidation potential referred to the vacuum level is the reorganization energy (ΔG_r) after one-electron oxidation reaction (Eq. 2). The values of E°_{ox} for alkylbenzenes used in the present work are not available because of their irreversible nature in CV both in acetonitrile[2] and nitrobenzene except for hexaethylbenzene. Therefore, the ΔG_r values can not be evaluated for most of the samples of this work. It is interesting, however, to point out that, according to the work by Kochi et al.,[2] the alkylbenzenes give reversible CV waves in trifluoroacetic acid. Therefore we have made great efforts to obtain PEE spectra of trifluoroacetic acid solutions, and yet could not obtain the spectra because of their high vapor pressure of the solvent. Kochi et al. also reported that the equilibrium oxidation potentials in trifluoroacetic acid E°_{ox}(TFA) correspond perfectly to the peak potentials E^p_{ox} measured in acetonitrile (at sweep rate of 100 mV s^{-1}) as $E^\circ_{ox}(\mathrm{TFA})=1.01\times E^p_{ox}-0.001$. We may presume that real equilibrium potentials of alkylbenzenes in acetonitrile must not be very different from the standard oxidation potentials in trifluoroacetic acid, nor from the peak potentials in acetonitrile reported by them. Under such an assumption, the peak potentials will be used instead of the standard potentials to extract the alkyl substitution effect on the reorganization energy.

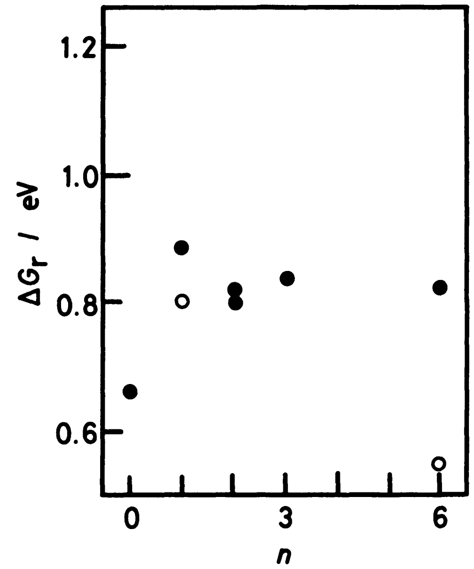

Fig. 6. The correlation of ΔG_r in acetonitrile and the number n of substituents introduced to benzene.

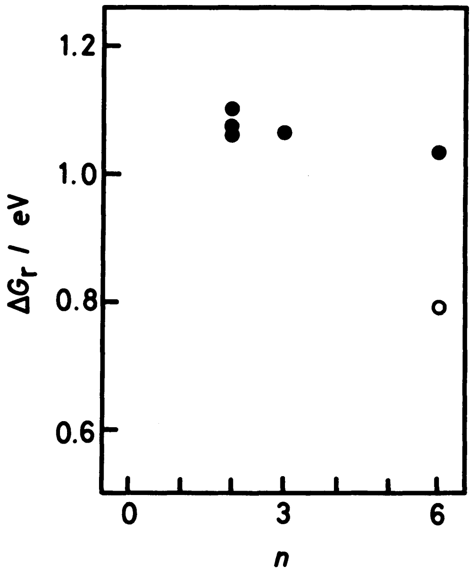

Fig. 7. The correlation of ΔG_r in nitrobenzene and the number n of substituents introduced to benzene.

Figures 6 and 7 show the correlation between ΔG_r so determined and n. The ΔG_r has no relation with n, but different alkyl group causes different ΔG_r value such as hexamethylbenzene/hexaethylbenzene or toluene/ethylbenzene.

It is noted that hexaethylbenzene has the smallest ΔG_r value, and displays totally reversible CV waves in both solvents. This fact may indicate that the reversibility of oxidation reaction of alkylbenzene depends on the degree of reorganization of the molecule.

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