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Photoionization Threshold Energies of Amine Solutions Studied by Photoelectron Emission by Solution

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The threshold energies E_t of photoelectron emission by solutions (PEES) were determined for several butylamines in acetonitrile and water. The correlations between E_t and gas-phase ionization potential I_P and oxidation potential E_{ox} were found to be linear. The difference between E_t and I_P originates from the electronic polarization energy of solvent molecules and the polarization energy was found to be inversely proportional to the solvation radius in accordance with the Born solvation free energy model. The E_t values were also compared with E_{ox} to discuss the reorientation relaxation of solvent molecules in the electron transfer process. The selective coverage of aqueous solution surface with amine molecule was indicated by the PEES technique.

The reactivity of an electron donor in solution is often estimated from its gas-phase ionization potential I_P or from the electrochemical oxidation potential E_{ox}. There are, however, many molecules which do not allow the measurement of I_P or E_{ox}. Low vapor pressure molecules of high molecular weight or ionic species present only in solvated state are almost out of the reach of the gas-phase UPS technique, while some molecules do not give clear oxidation wave owing to the limitations of availability of electrode material or supporting electrolytes, or to irreversible chemical reaction involved in the electron transfer reaction. The most controversial point on the use of I_P may be the complete neglect of solvation effects.

Although the UPS of solution samples have been measured for inorganic anions[1)] and organic molecules,[2)] the solvents used have been limited to the organic materials of the lowest vapor pressures.

The photoelectron emission by solution (PEES) experiment[3)] is a new technique which has been used to determine the external ionization potential I_P(ext) of solvated organic[4)] and inorganic anions[5)] and metal cations[6)] in aqueous solutions and it should be able to treat almost any solvent and any solvated species. The I_P(ext) can be obtained as the photoionization threshold energy E_t by using the PEES technique. The E_t for a molecule X corresponds to the energy change of the following reaction,

$$\mathrm{X(solv)} \rightarrow \mathrm{X^+(solv)} + \mathrm{e^-(vac)}. \qquad E_t \qquad (1)$$

The E_t is different from the internal ionization potential I_P(int) by the amount of V_0, the conduction band energy of the solvent referred to vacuum, and therefore, the reference level of the I_P(int) depends on the solvent while that of the E_t does not.

The I_P(int) corresponding to the following reaction,

$$\mathrm{X(solv)} \rightarrow \mathrm{X^+(solv)} + \mathrm{e^-(solv)}, \qquad I_P\mathrm{(int)} \qquad (2)$$

has been determined either by measuring photoconductance[7)] or by detecting solvated electron.[8)] The photoconductance measurement can be performed only with low conductance organic solvents and the detection of solvated electron involves rather complicated experiments. On the other hand, the E_t measurement by PEES can treat not only low conductance organic solvent but also high conductance ionic aqueous solution and the concept of the experiment is rather simple.

This work reports the E_t values for primary, secondary, and tertiary butylamines in acetonitrile and water to be compared with gas-phase I_P and E_{ox} in solution. Both I_P and E_{ox} are available for these amines and the character of their HOMO is well understood.[9)] The differences between E_t, I_P and E_{ox} will be interpreted in terms of their solvation radii and the reorientation of solvent molecules after the photoionization.

Experimental

The photoelectron emission spectra were obtained with a new instrument which is similar to the reported.[3a)] In this paper, only the modification from the original will be described.

1. The VUV monochromater used is Model 302-VM (λ-Minuteman Lab., Acton, Mass., USA), focal length; 20 cm, grating; 1200 lines/mm. The slit width was 1 mm.

2. Photoelectron current was detected by using a charge integrator instead of a lock-in amplifier. The charge integrator is an Electrometer Operational Amplifier (Keithley Model 301) having a feedback capacitor of 100 pF and a mercury relay switch to discharge the capacitor. The integration and the discharge were synchronized to the rotation of a glass wheel covered with sample solution. The integration time was normally 1 s during which the wheel rotated exactly 4 times.

3. In order to monitor the photon intensity a part of the photon beam just after the exit slit was accepted by a sodium salicylate film on the end (cut at 45° and polished) of a quartz optical fiber (1 mm dia.) which guided the converted UV light to a photomultiplier (Hamamatsu,

R647). The current from the photomultiplier was fed to another integrator which worked exactly in the same manner as the one for the photoelectron current.

4. A beam shutter driven magnetically from outside the lamp housing was placed between the hydrogen lamp and the entrance slit of the monochromater. The shutter was open for 1 s to measure photoelectron current and close for the same period to measure "dark current."

In order to get high photon flux relatively wide slit width was used. Therefore, all the E_t values were corrected according to the resolution of the monochromater.

The spectra were taken at −30 °C for acetonitrile solutions and at 1 °C for aqueous solutions. In order to discriminate the photoionization of gaseous molecules from that of solution, the spectra at several different temperatures were also obtained for the acetonitrile solutions.

This technique is rather insensitive to impurity and needs a relatively high concentration solution, 0.1—1 mol dm^{-3}. However, the aqueous solution was extremely sensitive to the contamination from surface active species. Therefore, the spectrum for aqueous solution was always obtained after a run with pure water to evaluate the contribution from contaminations.

The water content in acetonitrile used was determined by Karl Fischer titration method. Though the content varied from 12 to 54 mmol dm^{-3}, it did not cause any change in the PEE spectra of amines.

The gas-phase He(I)-UPS had also been carried out in this laboratory.[10]

Results

In Fig. 1 are shown the PEE spectra of 0.1 mol dm^{-3} butylamine in acetonitrile at different temperatures. The PEE spectra show the quantum yield Y of photoelectron emission per incident exciting photon at the energy of the photon $h\nu$. The spectrum of acetonitrile (curve D) is included to show that the photoionization of the solvent was not detected. As the solution is cooled down, the yield at high energy region decreases, but that between 8 and 8.5 eV increases. The yield current at higher photon energy (>8.6 eV) is concluded to be originated from the photoionization of gaseous amine molecules present in the space between the exit window of the monochromater and the solution, since the rising point of the curve A is very close to the adiabatic I_P for butylamine (8.62 eV). At the lower temperature, viz. in the lower gas pressures of the amine and acetonitrile, the photoelectron from the solution increases. This is the result of the reduction of photoelectron collision with the gaseous molecules. The PEE spectra were taken at the lowest possible temperature, i.e. −30 °C for acetonitrile solutions, and only low energy region of the spectrum (lower than gas I_P) was used to determine the threshold energy.

The threshold energy E_t is determined by using the extrapolation method based on the following equation by Brodsky-Tsarevsky,[11]

$$Y = (h\nu - E_t)^n, \tag{3}$$

where $h\nu$ is the exciting photon energy. The PEES study on aqueous solutions has been done successfully by plotting $Y^{1/n}$ against photon energy with n value of 2 or 2.5 to determine E_t as follows,[3b,3c]

$$Y^{1/n} = h\nu - E_t. \tag{4}$$

In the present study on amines, n value of 2.5 gave better linear plot than 2 for all of the PEE spectra obtained. An example of the $Y^{0.4}$ plot to determine E_t is shown in Fig. 2 for the curve A, the same spectrum as C in Fig. 1.

Although it has recently been reported that the shape of the photoelectron emission yield against photon energy should be affected by dielectric dispersion of the solvent,[12] the difference on E_t resulted from the use of 2 or 2.5 for n value amounted 0.1 eV normally and the difference, therefore, does not affect the present discussion.

The quantum yield from butylamine in acetoni-

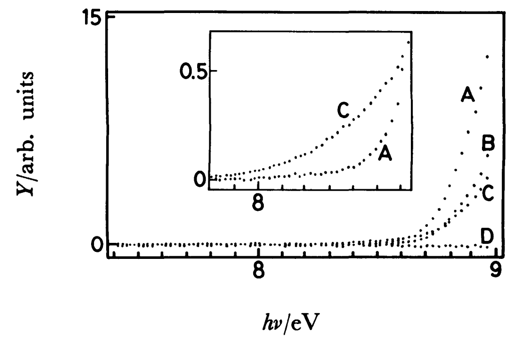

Fig. 1. PEE spectra of 0.1 mol dm^{-3} butylamine in acetonitrile taken at different temperatures. A: 1 °C, B: −10 °C, C: −30 °C, D: acetonitrile only at −30 °C.

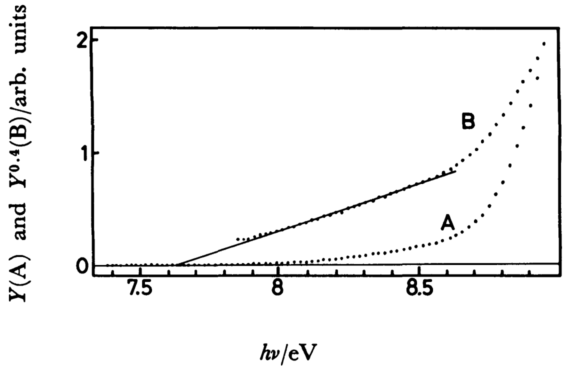

Fig. 2. PEE spectrum of 0.1 mol dm^{-3} butylamine in acetonitrile at −30 °C (A) and its $Y^{0.4}$ plot (B) to determine E_t.

trile solution is proportional to the concentration as shown in Figs. 3 and 4. In Fig. 3 are shown the yields at different photon energies, while the relation between the slope of the $Y^{0.4}$ plot and the concentration is shown in Fig. 4 by taking $(dY^{0.4}/dE)^{2.5}$ vs. concentration. In the figure are also included the E_t values determined at different concentrations. The yields for all the amines studied in acetonitrile were proportional to their concentrations, although the low solubility of tributylamine limited the highest yield at around 0.05 mol dm^{-3}.

Another example of PEE spectrum is shown in Fig. 5 for butylamine in water containing 10 mmol dm^{-3} KOH to suppress the protonation of the amine. It seems that the $Y^{0.4}$ plot is composed of two lines. One of them is drawn in the figure, which gives the E_t value of around 7.6 eV for the amine in water. The other corresponds to the ionization either of 10 mmol dm^{-3} OH$^-$ ion whose E_t has been reported to be 8.45 eV,[13] or of gaseous amine. The yield from butylamine in aqueous solution is not proportional to the concentration as shown in Fig. 6. The 1 mmol dm^{-3} solution gave almost the same spectrum as the 0.1 mol dm^{-3} solution. This fact indicates that the surface of aqueous solution is covered with butylamine molecule and that this spectroscopic technique is sensitive only to the surface of the solution. The E_t obtained for butylamine in water (7.7 eV) is the same as that in acetonitrile. The PEE spectra of secondary and tertiary butylamines in water gave E_t values similar to the I_P values for the corresponding gas molecules, therefore, they will not be reported here.

The E_t values determined were corrected for the resolution of the monochromater and are collected in Table 1 together with I_P and E_{ox} values, by He(I)-UPS[9,10] and cyclic voltammetry,[14] respectively.

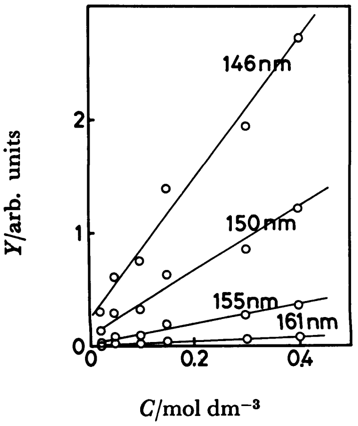

Fig. 3. Dependence of quantum yield Y on the concentration C of butylamine in acetonitrile at different exciting photon wave lengths. $T=-30$ °C.

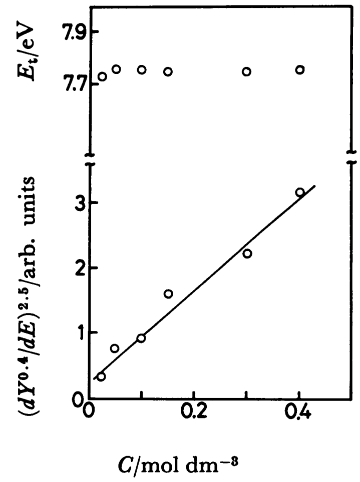

Fig. 4. Correlations between the slope of $Y^{0.4}$ plot and the concentration C shown as $(dY^{0.4}/dE)^{2.5}$ vs. C, and the threshold energy E_t and C for butylamine in acetonitrile. $T=-30$ °C.

Discussion

Correlation between E_t and I_P. The correlation

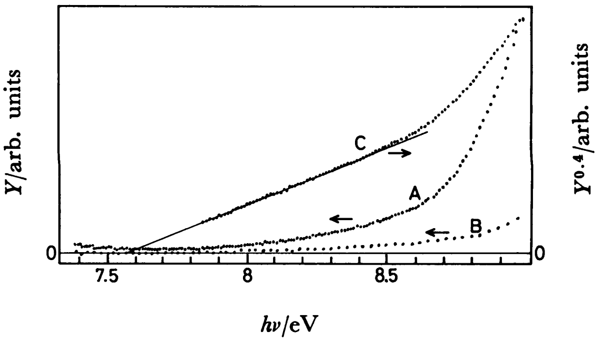

Fig. 5. PEE spectra of 0.1 mol dm^{-3} butylamine in 10 mmol dm^{-3} KOH aqueous solution (A) and 10 mmol dm^{-3} KOH aqueous solution (B). $Y^{0.4}$ plot for curve A is included (C). $T=1$ °C.

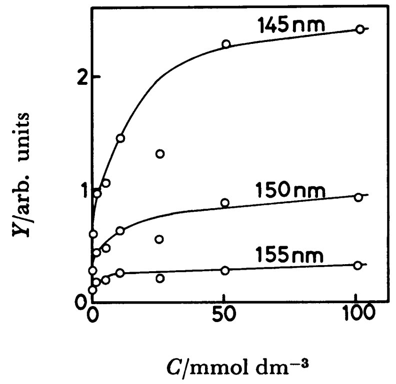

Fig. 6. Dependence of quantum yield Y for butylamine in 10 mmol dm^{-3} KOH aqueous solution at different exciting photon wave lengths upon the concentration C of the amine. $T=1$ °C.

Table 1. I_P, E_t and E_{ox} Values, and the Parameters Calculated for Acetonitrile Solutions

	I_{Pa}	I_{Pv}	E_t	$-P_+$	r	E_{ox}	$-R^{c)}$	$-R_{out}$
	eV	eV	eV	eV	nm	V	eV	eV
Butylamine	8.62	9.29	7.7_3	1.22	0.31[a] 0.27[b]	1.63	1.60	1.17
Isobutylamine	8.65	9.29	7.6_9	1.28	0.30[a] 0.27[b]	1.62	1.57	1.23
t-Butylamine	8.64	9.24	7.6_7	1.27	0.30[a] 0.27[b]	1.64	1.53	1.22
Dibutylamine	7.83	8.49	7.0_4	1.12	0.34[a] 0.32[b]	1.31	1.23	1.07
Diisobutylamine	7.77	8.47	7.0_4	1.08	0.35[a] 0.32[b]			
Tributylamine	7.20	7.88	6.6_8	0.86	0.44[a] 0.36[b]	1.02	1.16	0.82
Ethylenediamine	8.51	9.29	7.5_5	1.35	0.28[a] 0.23[b]			
Benzene	9.25	9.25	7.8_0	1.44	0.26[a] 0.26[b]			

a) Calculated from P_+. b) Calculated from densities at −30 °C. If the data are not available, they are estimated by extrapolating known values, Ref. 19. c) Calculated from E_t and E_{ox} ($-R=E_t-E_{ox}-4.5$). The 4.5 is to convert the value (vs. NHE) to the one referred to vacuum level.[26]

between E_t measured in acetonitrile and I_P in gas-phase was found to be linear,

$$E_t = 0.73 \times I_{Pa} + 1.40 \tag{5}$$

or

$$E_t = 0.74 \times I_{Pv} + 0.81, \tag{6}$$

where I_{Pa} and I_{Pv} are adiabatic or threshold and vertical ionization potentials for gaseous molecule, respectively. Therefore, the *photochemical* reactivity of the amine as an electron donor in acetonitrile can well be estimated from the gas-phase I_P values. The term *photochemical* is used here to distinguish vertical transition from adiabatic reaction process. Since I_P corresponds to the energy change of the following reaction,

$$X(\mathrm{vac}) \rightarrow X^+(\mathrm{vac}) + e^-(\mathrm{vac}), \qquad I_P \tag{7}$$

the difference (I_P-E_t) comes from the difference between solvation energies ΔG(solv) of X and X$^+$,

$$X(\mathrm{vac}) \rightarrow X(\mathrm{solv}), \qquad \Delta G(\mathrm{solv}) \tag{8}$$

$$X^+(\mathrm{vac}) \rightarrow X^+(\mathrm{solv}). \qquad \Delta G^+(\mathrm{solv}) \tag{9}$$

$$I_P - E_t = \Delta G(\mathrm{solv}) - \Delta G^+(\mathrm{solv}). \tag{10}$$

It has been known that there exists the surface potential at a gas/solution interface (0.08±0.06 V for water[15] and −0.10±0.06 V for acetonitrile[16]). Though the values of E_t and ΔG^+(solv) include the surface potential, the effect of the potential is cancelled in Eq. 10, because the potential which accelerates the escaping photoelectron from solution to gas phase also accelerates the incoming cation from gas phase into solution by the same amount. In any case, the surface potential is considered to be small and will be neglected in the present study.

Note that the species X$^+$(solv) which appears in Eqs. 1 and 9 is not completely solvated, because the photoionization leaves X$^+$ ion having the same solvation geometry as the neutral molecule X. Only the electronic polarization of the solvent molecules is induced by the photoionization of X. One, therefore, divides ΔG^+(solv) into ΔG(solv) and the polarization energy P_+,

$$\Delta G^+(\mathrm{solv}) = \Delta G(\mathrm{solv}) + P_+. \tag{11}$$

From Eqs. 10 and 11,

$$I_P - E_t = -P_+. \tag{12}$$

The polarization energy is frequently estimated by modifying the Born equation[17] for the electrostatic solvation energy of ion as follows,

$$P_+ = -(e^2/2r)(1-\varepsilon_{op}^{-1}), \tag{13}$$

where r is the radius of the central ion, ε_{op} the optical dielectric constant of the solvent. Since, as already mentioned, the geometry of X$^+$(solv) is quite the same as X(solv), r could be called the *radius of solvation sphere of the neutral molecule* X. Now we can obtain the r by using Eq. 13.

The problem one must answer for the use of Eq. 12 to obtain P_+ is whether the E_t value determined by the present method corresponds to adiabatic or vertical ionization process of the species in the solvent, or to somewhere else. We have obtained[18] a theoretical yield spectrum by use of Eq. 3 with an assumption that the density of states for amine molecules in solution is the same as that in gaseous phase, i.e. the Y was obtained by a convolution calculation of the gas-UPS band with Eq. 3. The UPS first band of butylamine pertaines to the ionization of nitrogen lone pair electron and is broad (0.83 eV in the half width). If the extrapolation to $Y^{0.4}=0$ on the theoretical yield curve is performed near to the threshold region, the E_t value comes close to I_{Pa}, while the extrapolation gives the value of I_{Pv} if the theoretical curve at far high energy region from I_{Pv} is used. In the higher energy region of the real PEE spectra there are other photoionization processes, e.g. the photoionizations of other species in the solution and the gaseous amine molecule. On the other hand, lower energy region is obscured by noise current. Therefore, the usable region for the extrapolation is limited to about 0.5 eV in the present study on amines. Our simulation calculation indicates that the extrapolation in the present study gives the E_t value corresponding to the midpoint of I_{Pa} and I_{Pv}. In the PEE studies by Delahay, the lenghth of the region for extrapolation used to determine E_t is almost 1 eV or even longer.[5] He considered the E_t obtained by his extrapolation method as the vertical ionization potential of the solute. In the present study we take the average of I_{Pa} and I_{Pv} as the I_P for gaseous amine to compare with E_t. Thus,

$$-P_+ = (I_{Pa} + I_{Pv})/2 - E_t. \quad (14)$$

The values of P_+ and r calculated by using Eq. 13 are included in Table 1. The ε_{op} in Eq. 13 is estimated to be 1.89[19] for acetonitrile at −30 °C.

The values of r should be used only to estimate the degree of solvation because of the following reason. Neither the geometrical shape nor the charge distribution on the amine cation is spherical. The density of the positive charge on the cation must be localized on the nitrogen atom, since the photoionization removes the nitrogen lone pair electron. The polarization energy is the function of the distance between charge center and solvent molecules, and the number of solvent molecules around the cation. We call the r most appropriately *effective* solvation radius.

The r of 0.25 nm is obtained for butylamine in water and is smaller than that in acetonitrile. The decrease of r in water could be interpreted in terms of the hydrogen bonds between the amine and water molecules. However, the fact that the amine molecule is deposited on the aqueous solution surface implies that such molecule must have smaller number of solvent molecules and thus larger effective solvation radius. We certainly need more knowledge of the solution structure of alkylamine to interpret the value of r.

Correlation between E_t and E_{ox}. Most of the butylamines studied in the present study can be oxidized electrochemically on a platinum electrode in acetonitrile. The oxidation potentials E_{ox} determined with cyclic voltammetry by Mann[14] are also included in Table 1. Since the cyclic voltammetry gives completely irreversible waves for the alkylamines, the E_{ox} values read at the peak position in the voltammograms are by no means equilibrium potentials thermodynamically meaningful and the values must depend on sweep rate and other experimental conditions.[25] In view of the present study, the E_{ox} values are considered to be the potentials at which the following one-electron oxidation reaction can take place at a rate comparable to that of diffusion process.

$$\mathrm{X(solv)} \rightarrow \mathrm{X^+(solv)} + \mathrm{e^-(electrode)}. \qquad E_{ox} \quad (15)$$

If the E_{ox} were of an equilibrium oxidation potential, the difference between E_t and the E_{ox} both referred to the common vacuum level[26] should be the reorganization energy for the electron transfer reaction 15.[3c] That is because E_t is the energy difference between solvated molecule X and the cation X^+ with the same molecular and solvation structures as the neutral molecule X, while E_{ox} is the energy difference between the X and the X^+ with the most stable molecular and solvation structures. Therefore the energy states for the cations X^+ in Eqs. 1 and 15 are not the same.

Due to the irreversibility in the alkylamine case, however, the interpretation of the difference ($E_t - E_{ox}$) is not straightforward, but should be as follows. The difference is the relaxation energy from the photoionized state which corresponds to the ion having the same molecular and solvation geometries as the neutral molecule, to the partially relaxed ionic state as for the molecular (inner) and solvation (outer) geometries which corresponds to the transition state of the electron transfer. The plot of E_{ox} vs. E_t gives a line with a slope of 0.58 as shown in Fig. 7. The difference ($E_t - E_{ox}$), containing the relaxation energy R to the transition state, is greater for the smaller amine. Since the molecular relaxation energies R_{in} estimated from ($I_{Pa} - I_{Pv}$) are almost the same (0.60—0.68 eV) for the amines studied, the difference reflects the outer relaxation R_{out}. Therefore, the reorientation energy of acetonitrile molecules around the smaller amine cation is greater.

The R_{out} for metal complex has been calculated for the studies on the PEE of aqueous solutions[5,20,21] by

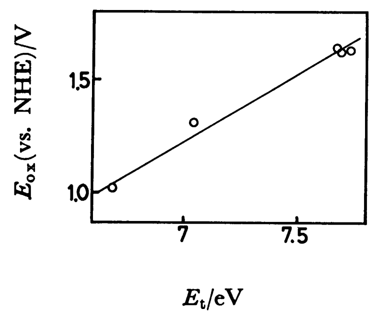

Fig. 7. Correlation between oxidation potential E_{ox} and threshold energy E_t of butylamines in acetonitrile. The data for E_{ox} are taken from Ref. 14.

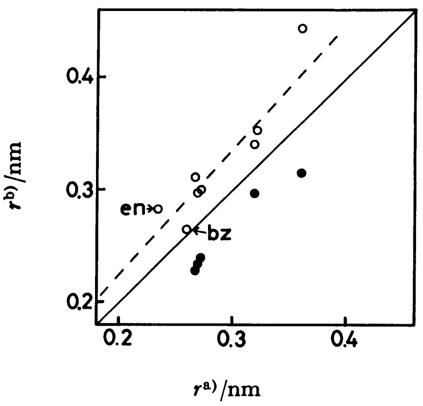

Fig. 8. Correlation between solvation radii determined from the densities of pure liquid $r^{a)}$ and PEE experiments $r^{b)}$; from polarization energy (○) and reorganization energy (●). The densities at −30 °C are estimated by extrapolating known values, Ref. 19. Solid line: slope=1, corresponding to k=0.5, broken line: the line corresponding to k=0.558, see the text. en: ethylenediamine, bz: benzene.

using the following equation,

$$R_{out} = -(e^2/2r)(\varepsilon_{op}^{-1} - \varepsilon_s^{-1}), \tag{16}$$

where ε_s is the static dielectric constant of solvent. The same equation has been used to calculate outer-sphere activation energy for electron exchange reactions.[22]

Since we already know the r value from polarization energy, the values of R_{out} can be calculated by using Eq. 16 and are listed in Table 1. The calculation concludes that most part of R comes from R_{out}.

Estimation of r. There are several different ways to estimate the value of r. Delahay[3c] calculated the r using the molecular density δ of pure material as follows,

$$r = k(m/\delta)^{1/3}, \tag{17}$$

where m is the molecular weight and k is $(3/4\pi)^{1/3}$ (=0.62). Inokuchi et al. have calculated the polarization energies for aromatic[23] and aliphatic[24] hydrocarbons using Eqs. 13 and 17 with k=0.5, and they obtained good agreement with experimental polarization energies for solid hydrocarbons. They also tried other r values but the agreement was poorer.

The r values determined from polarization energies and calculated by using Eq. 17 with k=0.5 are compared in Fig. 8. The result of Fig. 8 shows that the best linear relation between the r values is obtained at k=0.558. It was also found that the polarization energy obtained by taking I_P in Eq. 12 from I_{Pa} instead of $(I_{Pa}+I_{Pv})/2$ gave unreasonably large r values and, on the other hand, from I_{Pv} too small r. This fact is considered supporting our simulation calculation which indicates that the E_t values for amines are average ionization potentials for vertical and adiabatic processes.

Since the experimental value of (E_t-E_{ox}) seems to be almost equal to the outer relaxation energy, the estimation of r is attempted by taking $R_{out}=-(E_t-E_{ox})$ and by using Eq. 16 and the r values so obtained are plotted in Fig. 8. The agreement of the r values from the polarization and relaxation energies and from the densities implies that the Born approximation should be useful for a rough estimate of energetics of PEE process.

In the figure are added other experimental results for benzene and ethylenediamine. The added points lie on the same line as for amines. We have expected that these two molecules might behave in different way, because the butylamine cation has the electronic charge localized on the nitrogen atom, while the charge on benzene ion must be delocalized and two equivalent nitrogen atoms in ethylenediamine may contribute to the delocalization of cationic charge on the molecule. However, the experimental results show that the Born approximation could be applied to either of linear, plane or unsymmetrical molecule equally well. At the present stage, therefore, the PEES experiment can not predict how the charge produced by photoionization is distributed on the cation.

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