Vertical Ionization Potentials of Alkoxides in Solution

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The photoelectron-emission threshold energies were determined for aqueous and alcoholic solutions of potassium hydroxide and potassium metal. The energies correspond to the vertical ionization potentials of the solutes. The results are in accord with the fact that in alcohol-rich solutions the hydroxide ion reacts with alcohol to produce the alkoxide ion. The threshold energy for the alkoxide ion reflects the ionization potential of the alkoxide ion in a vacuum and the solvation effect. The difference in the ionization potential in a vacuum and in a solution, which is due to the solvation effect, was found to correlate with the acceptor number of the solvent.

It has recently been shown that the vertical ionization potential of nucleophile in solution is related to its S_N2 reactivity, i.e. the activation energy of the reaction correlates with the vertical ionization potential.[1)] The importance of the ionization potential of solvated species has also been recognized by Pearson; he has estimated the values for many molecules and ions from thermochemical data.[2)] However, the ionization potential in solution could not have been determined experimentally until photoelectron emission spectroscopy for solution (PEES) appeared.[3)]

In the present study, the vertical ionization potentials of alkoxide anions, which are important nucleophiles, were determined in alcohols by PEES as the photoelectron emission threshold energy (E_t). The E_t value for an anion is defined as

$$\mathrm{X^-(solv)} \rightarrow \mathrm{X^0(solv)} + \mathrm{e^-(vac)} \quad E_t. \tag{1}$$

Since $\mathrm{X^0(solv)}$ in Eq. 1 is the product of an optical process (Franck–Condon transition), $\mathrm{X^0(solv)}$ has a geometrical structure which is exactly the same as that of $\mathrm{X^-(solv)}$. Thus, the E_t value is of the vertical ionization potential. Since the E_t value reflects not only the ionization potential of $\mathrm{X^-}$ in the gas-phase, but also the stabilization energy of its negative charge by solvation, the important part of the solvation energy of an anion can be obtained from the E_t value. The solvent effects on the E_t values of alkoxide ions in the corresponding alcohols are compared with those for halide ions.

Experimental

Materials. The potassium hydroxide (assay; 85%, for semiconductor use) and the potassium metal used for preparing the solutions were of guaranteed reagent grade from Nacalai Tesque, Inc., Osaka and were used without further purification. The water was distilled, deionized, and purified further by using a Millipore system. Methanol, ethanol, 1-propanol, and 1-butanol of spectra-grade were fractionally distilled from CaH_2.

Sample Preparation. Sample solutions were prepared just before the measurements. Aqueous OH^- solutions were prepared by using KOH or K metal. The preparations of aqueous solutions with K metal were carefully carried out under a nitrogen atmosphere. For preparing alcoholic solutions, the solvents were deaerated before adding KOH or K metal, and every process was carried out under a nitrogen atmosphere. Because of the slow dissolution rates of KOH in 1-propanol and 1-butanol, powdered KOH was added.

The concentrations of the bases were determined by pH titration with sulfuric acid. The alcoholic solutions were diluted with water before titration.

The water contents in the alcoholic solutions used in this study were determined by Karl-Fischer titration analysis. The contents varied with the amounts of KOH used, and were independent of the amounts of K metal. The molar ratios of water to KOH were between 1.0—1.5, and those to K metal were between 0.3—0.7.

Photoelectron Emission Spectra. The spectrometer and the experimental methods have been described elsewhere.[4,5)] The PEE spectra were obtained at +1 °C for aqueous and at −30 °C for alcoholic solutions. The measurements were repeated several times at different base concentrations of 0.05—0.3 $\mathrm{mol\,dm^{-3}}$.

Results

The E_t values obtained for solutions of KOH or K metal in water and alcohols are given in Table 1. Both solutions prepared from KOH and K metal gave the same E_t values within the experimental error. The E_t values were found not to vary with the water contents in the present study. In each solvent system, the photoelectron emission yield was proportional to the concentration of the base in the 0.05—0.3 $\mathrm{mol\,dm^{-3}}$ range, and the E_t values were found not to depend on the concentration.

Discussion

For OH^- in alcohols, the following equilibrium is known:

$$\mathrm{OH^-} + \mathrm{ROH} \rightleftarrows \mathrm{H_2O} + \mathrm{RO^-} \tag{2}$$

$$K = \frac{[\mathrm{H_2O}][\mathrm{RO^-}]}{[\mathrm{OH^-}][\mathrm{ROH}]} \tag{3}$$

The values of equilibrium constant (K) have been determined by several methods.[6—10)] The K value of 13±3 was determined for a 1-butanol solution by ^{1}H NMR spectroscopy.[6)] This value predicts the molar ratio, $[\mathrm{OH^-}]/[\mathrm{RO^-}]=0.1$—$0.3$, for the present study. Ethanol solution was studied by means of indicator color

Table 1. Gas-Phase Ionization Potentials $I_{\rm p}$, Threshold Energies $E_{\rm t}$ (Solution-Phase Vertical Ionization Potentials), and Charge-Solvent Electrostatic Interaction Energies ΔE^- for Bases in Solvents

Solvent	$A_{\rm N}$ a)	Base	$I_{\rm p}$/eV	[$I_{\rm p}$/eV] f)	$E_{\rm t}$/eV	$-\Delta E^-$/eV
H_2O	54.8	OH^-	1.83 b)	[0.88]	8.26±0.05	6.43±0.05
		Br^-	3.36 b)		7.79 g)	4.43
		I^-	3.06 b)		7.05 g)	3.99
Methanol	41.3	CH_3O^-	1.57 c)	[1.31]	7.53±0.04	5.96±0.04
		Br^-	3.36 b)		7.61 g)	4.25
		I^-	3.06 b)		6.80 g)	3.74
Ethanol	37.1	$C_2H_5O^-$	1.73 d)	[1.34]	7.34±0.03	5.61±0.03
		Br^-	3.36 b)		7.32 g)	3.96
		I^-	3.06 b)		6.61 g)	3.55
1-Propanol	31.0	$C_3H_7O^-$	1.79 d)	[1.40]	7.13±0.03	5.34±0.03
		Br^-	3.36 b)		7.36 g)	4.00
		I^-	3.06 b)		6.61 g)	3.55
1-Butanol	30.0	$C_4H_9O^-$	1.79 e)	[1.40]	6.96±0.03	5.17±0.03

a) From Ref. 13. b) From Ref. 14. c) From Ref. 15. d) From Ref. 16. e) Calculated by PM3-MO method and correted. f) Calculated by PM3-MO method. g) From Ref. 12.

changes;7) it was found that 96% of the total base is of the form of ethoxide ion in a 0.1 mol dm^{-3} KOH ethanol solution. The K values were also calculated for several alcohols by comparing the concentrations of the reaction products of parallel reactions8) or by using the Gibbs energy of transfer;9,10) it was found that almost all of the anions were of the form of alkoxide ions in alcohol-rich co-solvents. In this work it was confirmed that all of the $E_{\rm t}$ values for (KOH+alcohol) solutions were the same as those for (K metal+alcohol) solutions. This indicates that alkoxide ions are predominant, even if about a 50% excess amount of water to that of OH^- is present. Thus, we conclude that photoelectrons from alcoholic solutions are from alkoxide ions.

The obtained $E_{\rm t}$ values reflect both the ionization potentials of the ions in a vacuum and the solvation effects. The ionization potential of an anion in a vacuum ($I_{\rm p}$) is the electron affinity ($E_{\rm A}$) of the corresponding neutral species:

$$X^-(\mathrm{vac}) \rightarrow X^0(\mathrm{vac}) + e^-(\mathrm{vac})$$

$$I_{\rm p}(= E_{\rm A} \text{ for neutral species}) \qquad (4)$$

Thus, combining Eqs. 1 and 4 and the following solvation processes relates $E_{\rm t}$ to $I_{\rm p}$:

$$X^-(\mathrm{vac}) \rightarrow X^-(\mathrm{solv}) \quad \Delta G^-_{\rm solv} \qquad (5)$$

$$X^0(\mathrm{vac}) \rightarrow X^0(\mathrm{solv}) \quad \Delta G^0_{\rm solv} \qquad (6)$$

and

$$E_{\rm t} = I_{\rm p} - \Delta G^-_{\rm solv} + \Delta G^0_{\rm solv}, \qquad (7)$$

where $\Delta G^-_{\rm solv}$ and $\Delta G^0_{\rm solv}$ are the solvation energies for the anion and the neutral species, respectively. The photoionization of X^- makes the electronic polarization of the solvent molecules disappear. Therefore, we regard here the solvation energy for an anion as comprising $\Delta G^0_{\rm solv}$ and the electrostatic interaction energy (ΔE^-) between the negative charge of the anion and the dipole moments of the surrounding solvent molecules, which are enhanced by the polarization effect.

$$\Delta G^-_{\rm solv} = \Delta G^0_{\rm solv} + \Delta E^- \qquad (8)$$

Combining Eqs. 7 and 8, thus, extracts ΔE^- from $E_{\rm t}$:

$$E_{\rm t} - I_{\rm p} = -\Delta E^- \qquad (9)$$

If the ΔE^- value does not vary much, one would expect the presence of a linear correlation between $E_{\rm t}$ and $I_{\rm p}$, which, in fact, was observed for some systems with organic molecules.5,11) However, the $E_{\rm t}$ values for alkoxide ions vary in reverse of the $I_{\rm p}$ change (Table 1), indicating a significant solvent effect on ΔE^- in the present system.

Our study concerning the $E_{\rm t}$ values of the iodide ion in various solvents showed a correlation12) of $E_{\rm t}$ with the Mayer–Gutmann's acceptor number ($A_{\rm N}$)13) of the solvent. The same correlation was also found for bromide. The $A_{\rm N}$ value has been considered to be a measure of the electrophilic ability of the solvent. A larger $A_{\rm N}$ value solvent stabilizes more the negative charge on the anion through the electron donor–acceptor or the hydrogen-bonding interaction; it therefore gives a larger $E_{\rm t}$ value for the anion. Thus, the $E_{\rm t}$ value for the anion is a solvent parameter having a similar character to that of $A_{\rm N}$.

The plot of $E_{\rm t}$ for the alkoxides against $A_{\rm N}$ in the present study is found to give an even better linear relationship than that for iodide or bromide. For the halide cases, since the $I_{\rm p}$ values in Eq. 9 are constants, the

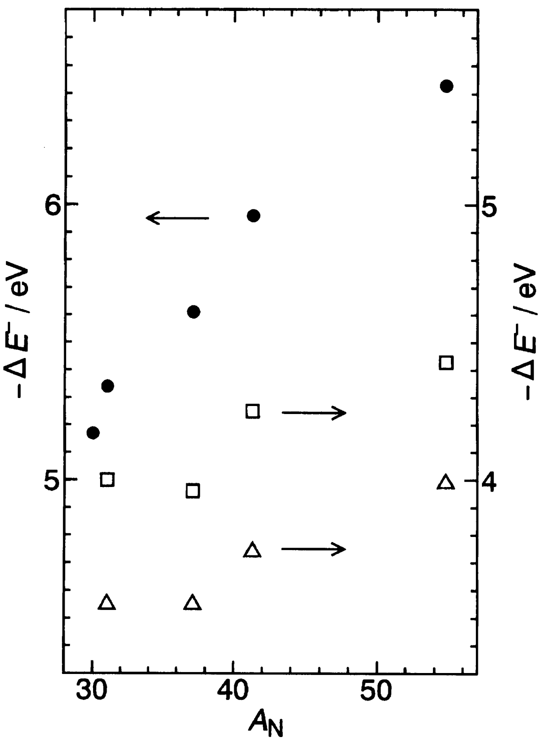

Fig. 1. Charge-solvent electrostatic interaction energies $-\Delta E^-$ vs. the acceptor number A_N for hydroxide or alkoxide (●), bromide (□), and iodide (△).

variation in ΔE^- directly appears in E_t. In this study, however, water contains OH^-, methanol CH_3O^-, ethanol $C_2H_5O^-$, and so on; thus, the I_p value of the anion varies with the choice of solvent. Therefore, in order to extract only the solvent effect on E_t for OH^- or alkoxide ions, the I_p values must be known.

Some of the I_p values in the gas phase for hydroxide[14)] or alkoxide ions[15,16)] have been known. However, since the value for the butoxide ion is not known, it was estimated by using a MNDO-PM3[17)] (Parametric Method 3) molecular-orbital calculation.[18)] The MO calculations were performed on the anion and the corresponding neutral radical, taking the same geometry as that of the anion which had been geometry-optimized. The I_p value was obtained from the difference in the total energies. Since the MO method predicted I_p values for $C_2H_5O^-$ and $C_3H_7O^-$ that are constantly smaller by 0.39 eV than their experimental ones, the I_p value for the butoxide ion was estimated by correcting the calculated value by the same amount.

The ΔE^- values obtained by Eq. 9 are plotted against A_N in Fig. 1, including the plots for iodide and bromide ions; the following points are definite:

(1) The ΔE^- correlates almost linearly with A_N.

(2) The change in ΔE^- for OH^- and alkoxide ions with A_N is greater than those for the halide ions.

(3) The alkoxide ions larger in size than the halide ions have greater ΔE^- values than do the halide ions.

The prediction of a greater charge stabilization energy for a smaller ion due to the electrostatic interaction is consistent with the variation of the ΔE^- values for I^-, Br^-, and OH^- in water and for I^- and Br^- in alcohols. Fact (3) implies, however, that the solvation mechanism for the alkoxide ion is different from that for the halide ion. Strong hydrogen-bonding must be formed between the oxygen in the alkoxide ion and the solvent alcohol compared to that between the halide ion and the solvent. This may simply be due to the smaller distance of hydrogen-bonding for the alkoxide ion. Solvent molecules come closer to the center of the negative charge in $RO^- \cdots HOR$ than in $Br^- \cdots HOR$ or $I^- \cdots HOR$, depending on their ionic radii.

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