BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (8), 2443—2444 (1979)

Oxidation-Reduction Equilibrium between Cation Radicals. An Approach to Determine Ionization Potentials of Electron Donor Molecules

Yôichi IIDA* and Akihiko YAMAGISHI
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received February 15, 1979)

Synopsis. For several electron donor molecules, the adiabatic ionization potential and the oxidation-reduction potential in the formation of cation radical from its parent molecule were estimated by using the equilibrium constant of a preferred electron transfer reaction from neutral donor molecule to another cation radical molecule in solution.

Earlier, we presented a method for determining electron affinity values of electron acceptor molecules by using preferred electron transfer (*i.e.*, oxidation-reduction) reaction between anion radicals in solution.[1] In this method, we measured the equilibrium constant of such reaction spectrophotometrically, so that we could estimate the difference of the oxidation-reduction potential and the electron affinity between two acceptor molecules.

In a similar way, if we observe chemical equilibrium of preferred electron transfer reaction from neutral electron donor molecule to another cation radical molecule in solution, we can obtain some knowledge regarding the ionization potentials of donor molecules as well as the oxidation-reduction potentials in the formation of their cation radicals. In the present paper, we apply this approach to several donor molecules with low ionization potentials such as *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD), *N,N*-dimethyl-*p*-phenylenediamine (DMPD), *N,N,N′,N′*-tetramethylbenzidine (TMB) and phenothiazine (PT).

In previous papers,[2] we examined the chemical equilibria of such preferred electron transfer reactions in various solvents. First, we shall derive oxidation-reduction potentials for those donor molecules. Hereafter, $E_1(\mathrm{M}^{+\cdot}, \mathrm{M})$, $E_2(\mathrm{M}^{+\cdot}, \mathrm{M})$, and $E_3(\mathrm{M}^{+\cdot}, \mathrm{M})$, (M= TMPD, DMPD, TMB, or PT), are denoted as reversible one-electron reduction potentials of $\mathrm{M}^{+\cdot}+\mathrm{e}\rightleftharpoons\mathrm{M}$ in (1: 3) ethanol–water solution, in aqueous solution and in acetonitrile solution, respectively.

The reaction between neutral phenothiazine and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine cation radical was examined in (1: 3) ethanol–water solvent. The oxidation-reduction equilibrium is expressed by

$$\mathrm{PT} + \mathrm{TMPD}^{+\cdot} \rightleftharpoons \mathrm{PT}^{+\cdot} + \mathrm{TMPD}. \tag{1}$$

If we neglect the effect of counter anions and assume that the activity coefficients of the solutes are unity, the equilibrium constant of this reaction is simply given by

$$K = \frac{[\mathrm{PT}^{+\cdot}][\mathrm{TMPD}]}{[\mathrm{PT}][\mathrm{TMPD}^{+\cdot}]}. \tag{2}$$

The equilibrium constant, K, was determined spectrophotometrically to be 0.96×10^{-6} at 10 °C. Using Nernst equation, we obtain a relation of reduction potentials, $E_1(\mathrm{PT}^{+\cdot}, \mathrm{PT})=E_1(\mathrm{TMPD}^{+\cdot}, \mathrm{TMPD})+0.34\,\mathrm{V}$.

In a similar way, we examined the following reactions and obtained the relations of reduction potentials. In the reaction between neutral phenothiazine and *N,N*-dimethyl-*p*-phenylenediamine cation radical in (1: 3) ethanol–water solution, $\mathrm{PT}+\mathrm{DMPD}^{+\cdot}\rightleftharpoons\mathrm{PT}^{+\cdot}+\mathrm{DMPD}$, $K=[\mathrm{PT}^{+\cdot}][\mathrm{DMPD}]/[\mathrm{PT}][\mathrm{DMPD}^{+\cdot}]=(3\pm1)\times10^{-5}$ at 10 °C, and $E_1(\mathrm{PT}^{+\cdot}, \mathrm{PT})=E_1(\mathrm{DMPD}^{+\cdot}, \mathrm{DMPD})+0.26\,\mathrm{V}$. From the relation between $E_1(\mathrm{PT}^{+\cdot}, \mathrm{PT})$ and $E_1(\mathrm{TMPD}^{+\cdot}, \mathrm{TMPD})$, we can estimate the relation, $E_1(\mathrm{DMPD}^{+\cdot}, \mathrm{DMPD})=E_1(\mathrm{TMPD}^{+\cdot}, \mathrm{TMPD})+0.08\,\mathrm{V}$. The reaction of $\mathrm{DMPD}+\mathrm{TMPD}^{+\cdot}\rightleftharpoons\mathrm{DMPD}^{+\cdot}+\mathrm{TMPD}$ was examined in two different solvents. In aqueous solution, $K=[\mathrm{DMPD}^{+\cdot}][\mathrm{TMPD}]/[\mathrm{DMPD}][\mathrm{TMPD}^{+\cdot}]=(2.8\pm0.6)\times10^{-2}$ at 10 °C and $E_2(\mathrm{DMPD}^{+\cdot}, \mathrm{DMPD})=E_2(\mathrm{TMPD}^{+\cdot}, \mathrm{TMPD})+0.087\,\mathrm{V}$, while in acetonitrile solution $K=(3.8\pm1.5)\times10^{-2}$ at 10 °C and $E_3(\mathrm{DMPD}^{+\cdot}, \mathrm{DMPD})=E_3(\mathrm{TMPD}^{+\cdot}, \mathrm{TMPD})+0.078\,\mathrm{V}$. For the reaction of $\mathrm{DMPD}+\mathrm{TMB}^{+\cdot}\rightleftharpoons\mathrm{DMPD}^{+\cdot}+\mathrm{TMB}$ in acetonitrile solution, $K=[\mathrm{DMPD}^{+\cdot}][\mathrm{TMB}]/[\mathrm{DMPD}][\mathrm{TMB}^{+\cdot}]=(3\pm1)\times10^{3}$ at 10 °C and $E_3(\mathrm{TMB}^{+\cdot}, \mathrm{TMB})=E_3(\mathrm{DMPD}^{+\cdot}, \mathrm{DMPD})+0.20\,\mathrm{V}$. From the relation between $E_3(\mathrm{DMPD}^{+\cdot}, \mathrm{DMPD})$ and $E_3(\mathrm{TMPD}^{+\cdot}, \mathrm{TMPD})$, we can further obtain $E_3(\mathrm{TMB}^{+\cdot}, \mathrm{TMB})=E_3(\mathrm{TMPD}^{+\cdot}, \mathrm{TMPD})+0.28\,\mathrm{V}$.

Although we obtained the reduction potentials of TMPD, DMPD, TMB and PT, the used solvents are different from each other. The reason for this is that we have to observe chemical equilibrium between cation radicals and that the stability of the cation radicals greatly depends on the solvents. Rigorously speaking, we cannot compare the values of the reduction potentials in different solvents, and only the comparison of the values in the common solvents is meaningful. However, as was shown above, the dependence of the $E_i(\mathrm{TMPD}^{+\cdot}, \mathrm{TMPD})-E_i(\mathrm{DMPD}^{+\cdot}, \mathrm{DMPD})$ value, (i=1, 2, or 3), on the solvents used appears to be within ±0.005 V.

Next, we consider the ionization potentials of TMPD, DMPD, TMB and PT on the basis of the above discussion. In a reversible one-electron addition to cation radical molecule, $\mathrm{D}^{+\cdot}$, to form neutral molecule, D, in solution, $\mathrm{D}^{+\cdot}+\mathrm{e}\rightleftharpoons\mathrm{D}$, the free energy change in the presence of mercury electrode is given by

$$\Delta G^\circ(\mathrm{D}) = -I_\mathrm{p}(\mathrm{D}) + \Delta\Delta G^\circ_{\mathrm{solv}}(\mathrm{D}, \mathrm{D}^{+\cdot}) + \chi_{\mathrm{Hg}}, \tag{3}$$

where $I_\mathrm{p}(\mathrm{D})$ is the ionization potential of the molecule, D, in gas phase, $\Delta\Delta G^\circ_{\mathrm{solv}}(\mathrm{D}, \mathrm{D}^{+\cdot})$ is the difference in free energy of solvation between D and $\mathrm{D}^{+\cdot}$, and χ_{Hg} is the electron work function of the mercury surface. Note that $I_\mathrm{p}(\mathrm{D})$ corresponds to an adiabatic ionization potential, because the reaction involves thermodynamical equilibrium. In the case of oxidation-reduction equilibrium between D_1 and $\mathrm{D}_2^{+\cdot}$ in solution, $\mathrm{D}_1+\mathrm{D}_2^{+\cdot}\rightleftharpoons\mathrm{D}_1^{+\cdot}+\mathrm{D}_2$, the observed equilibrium constant,

K, is related with ΔG°'s,

$$-RT\ln K = \Delta G^{\circ}(D_2) - \Delta G^{\circ}(D_1) = I_p(D_1) - I_p(D_2) + \Delta\Delta G^{\circ}_{solv}(D_2, D_2^{+\cdot}) - \Delta\Delta G^{\circ}_{solv}(D_1, D_1^{+\cdot}). \quad (4)$$

Therefore, if one assumes that the solvation energy, $\Delta\Delta G^{\circ}_{solv}(D_2, D_2^{+\cdot})$, is almost equal to $\Delta\Delta G^{\circ}_{solv}(D_1, D_1^{+\cdot})$, one can determine from Eq. 4 the difference of the ionization potentials between the D_1 and D_2 molecules. At the present time, although we have not enough knowledge regarding the solvation energy of neutral donor molecule and its cation radical, for neutral acceptor molecule, A, and its anion radical, $A^{-\cdot}$, the magnitude of $\Delta\Delta G^{\circ}_{solv}(A^{-\cdot}, A)$ is found to be hardly influenced by the species of the acceptor molecules, as long as the molecular sizes and the shapes are similar to one another.[1)]

Assuming $\Delta\Delta G^{\circ}_{solv}(D_1, D_1^{+\cdot}) \approx \Delta\Delta G^{\circ}_{solv}(D_2, D_2^{+\cdot})$, we will discuss the ionization potentials of TMPD, DMPD, TMB and PT in the following. So far, the ionization potential of TMPD has been studied in most detail.[3,4)] Therefore, if the value is one given for I_p(TMPD), the absolute values of I_p(DMPD), I_p(TMB), and I_p(PT) will be determined from Eq. 4 and the observed equilibrium constants. Photoionization of TMPD in gas phase was measured by Batley and Lyons and later by Nakato *et al.*[3,4)] The energy for onset of photoionization curve was assumed to correspond to the adiabatic ionization energy, but the onset was rather gradual in the case of TMPD. Batley and Lyons estimated the upper limit of the adiabatic ionization potential as $I_p(\text{TMPD}) \leq 6.25$ eV, while Nakato *et al.*, $I_p(\text{TMPD}) \leq 6.20$ eV. In the present paper, referring to Nakato's value, we take $I_p(\text{TMPD}) = 6.20$ eV as a standard. Then, by the use of the observed equilibrium constants of oxidation-reduction reactions, together with Eq. 4, the adiabatic ionization potentials of DMPD, TMB, and PT were estimated to be 6.28 eV, 6.48 eV, and 6.54 eV, respectively.

On the other hand, in Table 1, we compare the data with those measured by photoionization method. As has been mentioned, because of gradual onset of photoionization, it is rather difficult to determine exactly the adiabatic ionization energies by photoionization method, where only the upper limits of the ionization energies were estimated. In particular, the onset of ionization of phenothiazine is more gradual than the other diamine compounds. For each of the compounds, however, a fairly good agreement of the adiabatic ionization energies was obtained between the oxidation-reduction equilibrium method and the photoionization method. The order of the adiabatic ionization potentials was estimated as $I_p(\text{TMPD}) < I_p(\text{DMPD}) < I_p(\text{TMB}) < I_p(\text{PT})$ by our method, while in photoionization it appears that $I_p(\text{TMPD}) < I_p(\text{TMB}) \lesssim I_p(\text{DMPD}) < I_p(\text{PT})$. As for the magnitudes of I_p(DMPD) and I_p(TMB) in photoionization, the former value was measured by Nakato *et al.*,[4)] while the latter, by Batley and Lyons.[3)] Therefore, we consider that systematic determination of the I_p(DMPD) and I_p(TMB) values in photoionization is desirable to compare those values with ours.[6)]

Table 1. Adiabatic and vertical ionization potentials (eV) of electron donor molecules

Compound	Adiabatic ionization potential	Vertical ionization potential	Reference
N,*N*,*N′*,*N′*-Tetramethyl-*p*-phenylenediamine	≤6.20	6.75	Ref. 4
	≤6.25	6.47	Ref. 3
N,*N*-Dimethyl-*p*-phenylenediamine	≤6.46	6.97	Ref. 4
	6.28		This work
N,*N*,*N′*,*N′*-Tetramethylbenzidine	≤6.40	6.55	Ref. 3
	6.48		This work
Phenothiazine	<7.0	7.38	Ref. 3
		7.26	Ref. 5
	6.54		This work

In Table 1, the data on vertical ionization energies are also given for purposes of comparison. Usually, vertical energies exceed adiabatic energies because of a change of shape of the molecule upon ionization. The difference between the adiabatic and vertical energies is considerable in DMPD and PT, where it amounts up to 0.7 eV. This implies a considerable structural change upon ionization in those molecules. For example, the molecular structure of neutral PT is of bent form, while its cation radical may become planar.[7,8)]

So far, photoionization method in gas phase has been widely used to determine vertical ionization potentials of a number of organic molecules, but has some difficulties in obtaining adiabatic ionization potentials. Alternatively, the present approach of oxidation-reduction equilibrium is a useful method to determine adiabatic ionization potentials of such molecules. One of the difficulties of this method lies in the assumption of $\Delta\Delta G^{\circ}_{solv}(D_1, D_1^{+\cdot}) \approx \Delta\Delta G^{\circ}_{solv}(D_2, D_2^{+\cdot})$ in Eq. 4. The problem of the solvation energies of neutral molecule and its cation radical should be solved in order to obtain more exact adiabatic ionization potentials of a number of electron donor molecules.

References

1) Y. Iida and H. Akamatu, *Bull. Chem. Soc. Jpn.*, **40**, 231 (1967); Y. Iida, *Bull. Chem. Soc. Jpn.*, **44**, 1430 (1971); **49**, 3691 (1976); **52**, 1875 (1979).

2) A. Yamagishi, *Bull. Chem. Soc. Jpn.*, **48**, 3475 (1975); A. Yamagishi, *Chem. Lett.*, **1975**, 595.

3) M. Batley and L. E. Lyons, *Mol. Cryst.*, **3**, 357 (1968).

4) Y. Nakato, M. Ozaki, A. Egawa, and H. Tsubomura, *Chem. Phys. Lett.*, **9**, 615 (1971).

5) L. N. Domelsmith, L. L. Munchausen, and K. N. Houk, *J. Am. Chem. Soc.*, **99**, 6506 (1977).

6) In oxidation-reduction equilibrium method, we assume a constant value of $\Delta\Delta G^{\circ}_{solv}(D, D^{+\cdot})$, and the assumption will be justified as long as the sizes and shapes of molecules are similar. However, the size of TMB molecule is rather bigger than those of TMPD and DMPD molecules, and the $\Delta\Delta G^{\circ}_{solv}(\text{TMB}, \text{TMB}^{+\cdot})$ value may be different from the $\Delta\Delta G^{\circ}_{solv}(\text{TMPD}, \text{TMPD}^{+\cdot})$ or $\Delta\Delta G^{\circ}_{solv}(\text{DMPD}, \text{DMPD}^{+\cdot})$ value. This may be a reason why the I_p(TMB) value derived from our method is somewhat greater than the value obtained from photoionization method.

7) Y. Matsunaga and K. Shono, *Bull. Chem. Soc. Jpn.*, **43**, 2007 (1970).

8) J. D. Bell, J. F. Blount, O. V. Briscoe, and H. C. Freeman, *Chem. Commun.*, **1968**, 1656; J. M. Lhoste and F. Tonnard, *J. Chim. Phys.*, **63**, 678 (1966).