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The Electron Affinity of Methylene Blue in the Gas Phase

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ABSTRACT

The adiabatic electron affinity of Methylene Blue is identical with the adiabatic ionization energy of the methylene blue radical, which has been measured by photoionization and found to be 5·3 (±0·3) eV. This value is 0·4 eV lower than the vertical electron affinity of Methylene Blue.

1 INTRODUCTION

Most of the known electron affinities (EA) of organic compounds having π-electrons have been obtained from their half-wave potentials $E_{1/2}$ for one-electron reduction in comparison with $E_{1/2}$ of a reference substance and its measured EA in the gas phase.[1,2] Anthracene was usually used as the reference compound. An EA value estimated in this way is around 4 eV lower than the difference between the ionization energy (IE) and the first excited electronic state (ΔE_1). In order to obtain another reference, the EA of Methylene Blue MB^+ was calculated from $E_{1/2}$ ($MB^+/MB^\cdot$) in CH_3CN,[3] from the threshold energy of photoionization of the methylene blue radical $MB^\cdot$ in hexane[4] and from the enthalpy of the reaction of $MB^\cdot$ with Wursters blue radical $TMPD^{\cdot+}$ in CH_3CN.[5] The estimation of EA(MB^+) from measurements by these different methods yields EA(MB^+) = 5·8 eV, a value which is in agreement with eqn (1).

$$EA(MB^+) = IE(MB^+) - \Delta E_1(MB^+) \qquad (1)$$

In spite of this agreement it must be noted that there is an uncertainty caused by the unmeasurable single ionic solvation energy, which must be included in the calculation of EA from data measured in solvents. In order to examine these calculations, the measurement of IE($MB^{\cdot}$) = EA(MB^+) in the gas phase is necessary.

The photoionization threshold energy leads to the adiabatic ionization energy (IE_a) which is lower than the vertical ionization energy (IE_v).

2 EXPERIMENTAL

Photoionization currents were measured with a Keithley electrometer model 616. The monochromatized radiation from a 30-Watt deuterium lamp was directed between two gilt electrodes. The photon flux at 240 nm was measured with Leucomalachite Green as an actinometer.[6] This value was used to obtain the photon flux at the other wavelengths, in comparison with the fluorescence of sodium salicylate.[7] $MB^{\cdot}$ was prepared by electrochemical reduction of MB^+. The half-lifetime of $MB^{\cdot}$ in CH_3CN was found to be $2{\cdot}5 \times 10^6$ s. No disproportionation of $MB^{\cdot}$ could be found photometrically after holding at 87°C for 1 h in vacuo.

3 RESULTS AND DISCUSSION

Table 1 shows the relationship between photocurrents and quantum yields of $MB^{\cdot}$ with the wavelengths of irradiation. The temperature of $MB^{\cdot}$ at the bottom of the evacuated cell was held at 87°C. The onset of the photocurrent was at ≃250 nm, or equivalent to the photon energy at 4·96 eV. Measurements of threshold energy in electric fields between 0·5 V cm^{-1} and 5·0 V cm^{-1} yielded the relatiohship:

$$IE_a(MB^{\cdot}) = 5{\cdot}3(\pm 0{\cdot}3)\text{eV} = EA_a(MB^+).$$

Using different liquid filter solutions, such as H_2O, 10% H_2SO_4/H_2O, 10% KCl/H_2O and 10% KBr/H_2O, instead of a monochromator, allowed the measurement of photocurrents even when $MB^{\cdot}$ was held at room temperature. No photocurrents could be found with acetic acid as filter, this compound cutting off radiation at $\lambda < 250$ nm. It follows, therefore, that: $IE_a(MB^{\cdot}) = 5{\cdot}0$ eV.

IE_v ($MB^{\cdot}$) can be estimated from the measured IE_a ($MB^{\cdot}$) according to eqn (2) in which TMPD denotes *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine.

$$IE_v(MB^{\cdot}) - IE_a(MB^{\cdot}) = IE_v(\text{TMPD}) - IE_a(\text{TMPD}) \qquad (2)$$

IE_a (TMPD) was measured in this work to be 6·0 eV. Reported literature values for IE_v (TMPD) are 6·2 eV;[2] 6·5 eV[1] and 6·75 eV,[8] respectively.

TABLE 1
Relationship between the Quantum Yields ϕ of the Photocurrents of $\mathrm{MB}^{\cdot}$ and Wavelengths λ

λ (nm)	$i \times 10^{13}$ (Å)	$z \times 10^{-12}$ (s^{-1})	$\phi \times 10^{6}$
200	(2·84 ± 0·08)	0·08	22·2
210	(2·77 ± 0·03)	0·19	9·1
218	(2·38 ± 0·02)	0·38	3·9
220	(2·08 ± 0·01)	0·43	3·0
225	(1·81 ± 0·06)	0·56	2·0
230	(1·37 ± 0·09)	0·70	1·2
235	(1·08 ± 0·01)	0·87	0·8
240	(0·73 ± 0·02)	1·00	0·5
245	(0·38 ± 0·03)	1·13	0·2
250	(0·25 ± 0·15)	1·26	0·1

Temperature of $\mathrm{MB}^{\cdot}$ on the bottom of the cell = 87°C; electric field = 0·5 V cm^{-1}; z = number of photons × s^{-1}. Within the range of $200 \text{ nm} \leq \lambda \leq 240 \text{ nm}$, $E = a + b \ln \phi$ is valid; correlation coefficient = 0·999; a, b = constant and E = energy of the photons.

Using IE(TMPD) = 6·5 eV, and the measured values obtained in this present work for $\mathrm{IE_a}$(TMPD) and $\mathrm{IE_a}(\mathrm{MB}^{\cdot})$ it follows from eqn (2) that $\mathrm{IE_v}(\mathrm{MB}^{\cdot}) = 5{\cdot}7 \text{ eV} = \mathrm{EA_v}(\mathrm{MB}^{+})$.

The estimation of $\mathrm{IE_v}(\mathrm{MB}^{\cdot})$ derived from experimental $\mathrm{IE_a}(\mathrm{MB}^{\cdot})$ in the gas phase according to eqn (2) implies that there is an equal difference of $[\mathrm{IE_v} - \mathrm{IE_a}]$ for both the molecules $\mathrm{MB}^{\cdot}$ and TMPD. This is most probably valid on structural grounds. The principal result of this present investigation is expressed in the unusually high value of $\mathrm{IE_a}(\mathrm{MB}^{\cdot}) = \mathrm{EA_a}(\mathrm{MB}^{+})$ measured in the gas phase. This result would not be significantly changed even if the deviation from the difference $[\mathrm{IE_v} - \mathrm{IE_a}]$ for both molecules were around 0·5 eV.

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