Polarographic Half-Wave Reduction Potentials of Vinyl Compounds and their Molecular Orbital Computation

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The polarographic half-wave reduction potentials of several vinyl compounds have been determined under essentially identical condition*, and it has been found that these potentials are linearly related to the heights of the lowest vacant π-electronic energy levels of these compounds calculated by the LCAO MO method.

The reduction potentials were determined in a 3:1 dioxane-water mixture containing 0.05 M tetra-*n*-butylammonium iodide as a supporting electrolyte. All the compounds were purified by appropriate methods before use. A measured amount of vinyl compound was dissolved into the electrolyte solution so that its concentration was in the region ranging from 10^{-3} to 5×10^{-3} M.

The electrolysis-cell was immersed in a thermostat maintained at 25.0±0.1°C, and any oxygen dissolved in the solution was removed by passing through it a slow stream of oxygen-free and solvent-saturated nitrogen. The dropping-mercury electrode was polarized against a saturated calomel electrode (S. C. E.) connected to the mercury cathode through a pin-hole in the wall of the cell, and the current-voltage curve was recorded. Maxima of the current-voltage curves were suppressed by 10^{-5} M methylene blue incorporated in the sample solution. The half-wave potentials, $E_{1/2}$, were read against S. C. E. and were all corrected for *iR* drop. When tetra-*n*-butylammonium hydroxide was used as the supporting electrolyte, the potentials did not appreciably deviate from those determined in the iodide solution. All the obtained data on $E_{1/2}$ are listed in Table I.

In calculating the energies of the lowest vacant π-levels, the simple LCAO MO method (neglecting overlap integrals) was employed. For each vinyl compound x_{lv}, defined as $\varepsilon_{lv}=\alpha+x_{lv}\beta$, was obtained from the required secular equation. Here α and β are the Coulomb integral of a carbon atom and the resonance integral of a carbon-carbon π-bond, respectively, and ε_{lv} is the energy of the lowest vacant π-level. To empirical integral parameters associated with heteroatoms, were assigned the same values that had previously been used to calculate the localization energies of vinyl compounds[1,2]: $\alpha_O=\alpha+2\beta$ (for carbonyl oxygens), $\alpha_O=\alpha+\beta$ (for ethereal oxygens), $\alpha_N=\alpha+\beta$, $\alpha_{Cl}=\alpha+1.8\beta$, $\alpha_C=\alpha-0.2\beta$ (for carbons bearing a methyl group), $\beta_{CO}=\sqrt{2}\,\beta$ and $\varepsilon=0.1$**. The

TABLE I. THE INTERRELATION AMONG $E_{l/2}$, x_{1v} AND L_β^- FOR VINYL COMPOUNDS

Vinyl compound	$-E_{l/2}$ [a]		$-x_{lv}$	L_β^- [b]
	With Bu_4NI	With Bu_4NOH		
Acrylonitrile	2.01	1.95	0.314	1.240
Acrolein	1.53	—	0.315	1.214
Methyl vinyl ketone	1.67	1.63	0.386	1.299
Methyl acrylate	1.95	1.94	0.500	1.428
Methyl methacrylate	2.01	2.00	0.511	1.511
Styrene	2.35	2.35	0.662	1.704
α-Methylstyrene	2.39	2.39	0.692	1.843
β-Methylstyrene	2.54[c]	—	0.735	—
Phenyl vinyl ether	3.0	3.0	0.960	2.196
Ethylene	NW	NW	1.000	2.000
Vinyl acetate	NW	NW	1.065	2.130
Vinyl chloride	NW	NW	1.087	2.173
Propylene	NW	NW	1.105	2.210
n-Butyl vinyl ether	NW	NW	1.194	2.387
i-Butyl vinyl ether	NW	NW	1.194	2.387
Isobutylene	NW	NW	1.220	2.440

a) Given in volt vs. S. O. E. The mark NW means "no reduction wave".

b) Given in units of $-\beta$. The values are taken from Ref. 2.

c) H. A. Laitinen and S. Wawzonek, *J. Am. Chem. Soc.*, **64**, 1765 (1942).

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* Some experimental data determined under different conditions are available, which can not be directly compared.

[1] T. Fueno, T. Tsuruta and J. Furukawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1075 (1957).

[2] T. Fueno, T. Tsuruta and J. Furukawa, ibid., **78**, 1080 (1957).

** A carbon atom bearing one or more heteroatoms was assumed to have the Coulomb integral of $\alpha+\varepsilon\beta\Sigma k_X$. Here $\alpha+k_X\beta$ is the Coulomb integral of the heteroatom X.

resonance integrals for π-bonds other than carbonyl bonds were all assumed equal to β. The calculated values of x_{lv} are also listed in Table I. Since both α and β are negative quantities, the lowest vacant level ought to be more stable as x_{lv} takes a smaller negative value.

Inspection of the data given in Table I shows that, the smaller the value of x_{lv} for a vinyl compound, the more easily it can be reduced. Phenyl vinyl ether was found to have the highest reduction potential (ca. -3.0 V.) of all the compounds which could be reduced under the present experimental condition. At about -3.0 V. the residual current began to increase markedly owing to reduction of the supporting electrolyte. Vinyl acetate, vinyl chloride, *n*-butyl vinyl ether, *i*-butyl vinyl ether, ethylene, propylene and isobutylene gave no reduction waves in the range of the applied potential less negative than -3.0 V. vs. S. C. E. The situation may reasonably be explained by their relatively large values of $-x_{lv}$.

The half-wave potentials, $E_{1/2}$, determined with the ammonium iodide as the supporting electrolyte were found to be linearly correlated to x_{lv}'s by

$$E_{1/2} = 2.33\, x_{lv} - 0.80$$

the correlation coefficient being 0.995. The linear equation gives $\beta = -2.33$ eV., if it is assumed that, as in the case of unsaturated hydrocarbons[3,4], the electron transfer step from the electrode to vinyl compounds would be potential-determining. This value of β is in reasonable agreement with -2.23 eV.[4] for unsaturated hydrocarbons.

It seems interesting to note that the value of $-x_{lv}$ increases with increasing magnitude of the anionic β-carbon localization energy, L_{β}^{-}[2], of vinyl compounds, as seen in Table I. Thus, the polarographic reducibility of vinyl compounds may roughly parallel to their anionic polymerizability. This is to be expected, because vinyl compounds probably possess parallel susceptibilities toward an electron as well as basic substances. The detailed discussion on the present results will be published elsewhere.

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[3] H. A. Laitinen and S. Wawzonek, *J. Am. Chem. Soc.*, **64**, 1765 (1942).

[4] G. J. Hoijtink and J. van Schooten, *Rec. trav. chim.*, 72, 903 (1953).