Successive Electron Transfers to Molecules with Identical Interacting Centers — The Electroreduction of α,ω-9,9′-Dianthrylalkanes

By

Kingo Itaya, Allen J. Bard

Department of Chemistry, The University of Texas at Austin,
Austin, Texas 78712

and

Michael Szwarc

Department of Chemistry, State University of New York,
College of Environmental Science and Forestry, Syracuse, New York

The electrochemical behavior of α,ω-9,9′-dianthrylalkanes has been investigated in a 1:1 benzene-ACN mixture by cyclic voltammetry at a platinum electrode. The two successive electron transfer reactions of dianthrylalkanes merge into a single wave with the difference in cathodic and anodic peak potentials approaching that for a reversible one-electron transfer with increasing length of the methylene chain. The wavelength of the $0-0$ absorption and fluorescence bands and relative fluorescence quantum yield were obtained. Electrogenerated chemiluminescence (ECL) of the compounds in the presence of 10-methylphenothiazine (10-MP) is also described.

Das elektrochemische Verhalten von α,ω-9,9′-Dianthrylalkanen wurde an Platin in einem Benzol-ACN-Gemisch mit Hilfe zyklischer Voltammetrie untersucht. Die beiden nacheinanderfolgenden Elektronentransferreaktionen der Dianthrylalkane verschmelzen zu einer einzigen Welle, deren Potentialdifferenz von kathodischer zu anodischer Stromspitze mit ansteigender Methylenkettenlänge dem eines reversiblen Ein-Elektronenübergangs nahekommt. Die Wellenlänge der $0-0$-Absorption und Fluoreszenzbanden sowie die relative Fluoreszenzquantenausbeute werden bestimmt. Die elektrochemische Lumineszenz (ECL) der Verbindungen in Gegenwart von 10-Methylphenothiazin (10-MP) wird ebenfalls beschrieben.

Introduction

The problem of successive electron transfers to (or from) two or more identical electroactive centers on a molecule has been studied in organic
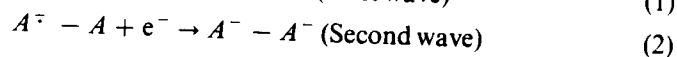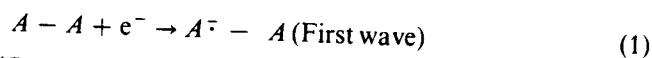
Experimental

Results and discussion

Voltammetry

The solubility of the compounds in ACN was too small to prepare solutions of appropriate concentrations, so all of the studies reported here were carried out in a 1:1 benzene-ACN mixture. The cyclic voltammograms of $n = 0, 2, 4, 6$ in 0.1 M TBAP-benzene-ACN mixture are shown in Fig. 1. The $n = 0$ compound clearly showed two distinct one-electron waves with a separation of the first and second formal potentials of about 270 mV. This result shows that the repulsive energy between the two electrons in the anti-bonding orbitals of each anthracene moiety is quite large compared with the other compounds, as discussed below, but it is still small with respect to the corresponding difference for anthracene itself [19, 20]. Moreover, the potential of the first reduction step for the $n = 0$ compound is well positive of that of 9-methylanthracene in the same solvent (Table 1) which also indicates a lowering of the energy of the anti-bonding orbital of an anthracene moiety in bianthryl by electronic interaction with the other anthracene. Note that these results are quite different from those reported by Hoijtink [21]. Considering the above argument, the reaction mechanism can be formulated as in Eqs. (1) and (2):

$$A - A + e^- \rightarrow A^{\cdot -} - A \text{ (First wave)} \tag{1}$$

$$A^{\cdot -} - A + e^- \rightarrow A^- - A^- \text{ (Second wave)} \tag{2}$$

where $A - A$ represents bianthryl.

For $n = 2$, the potentials for the two successive electron transfer reactions are much closer together (100 mV); the potential of the first wave is close, but still positive of, that for the reduction of 9-methylanthracene. Williams et al. [22] have studied the electrochemistry of diarylalkanes and paracyclophanes in DMF and reported a difference of peak potentials between the successive waves of about 150 mV for the $n = 2$ compound. For $n = 4$ and $n = 6$, the two successive electron transfer reactions are completely merged into a single

Table 1. Electrochemical and photochemical data of 2,0-dianthrylalkanes in Benzene-TCA

Compounds	$-E_p$[a] (Volt vs. SCE)	ΔE_p[c] (mV)	(0-0) band max (nm)		[d] (9-MA)
			absorption	fluorescence	
9-Methyl-anthracene	2.08₆	63	388	398	1.0
$n = 0$	1.97₅ (2.24₅)[b]	60	391	—	1.2
$n = 2$	2.02₅ (2.12₅)[b]	~65	395	403	0.019
$n = 4$	2.12₃	80	391	600	0.85
$n = 6$	2.10	65	389	398	1.26

[a] Cathodic peak potentials.
[b] Peak potential for second cathodic wave.
[c] Peak potential separation of first wave.
[d] Relative fluorescence quantum yield.

second electron transfer by the separation between the waves. In general a positive shift in the potential of the first reduction wave will be observed if the two electrophores interact so as to cause a lowering of the energy of the lowest antibonding orbital, as mentioned above. This situation is clearly observed for the $n = 0$ and $n = 2$ compounds, with the interaction of the $n = 2$ probably occurring "through space" rather than through the methylene chain. The potentials for the first waves of the $n = 4$ and $n = 6$ compounds are very close (and even slightly negative of) that for 9-methylanthracene, indicating that the two electrophores in these molecules are completely independent.

For the second electron transfer (formation of the dianion) energy for the coulombic repulsion between the two electrons in each electrophere is the major source of the difference in potentials between the first and second waves for the molecules which have two independent moieties ($n = 4$ and $n = 6$). This repulsion energy seems to be negligibly small for the $n = 6$ species. For example, if two negative charges are localized at the ends of a methylene chain of $n = 6$, the distance between them is about 9 Å. This leads to a static repulsion energy of about 0.05 eV in a medium with a dielectric constant of 30. Considering that the actual charge distribution in the anthracene ring is delocalized, the actual repulsion energy should be much smaller than the above value. For this reason the successive electron transfer reactions should occur with no difference in energy for $n = 6$ as observed experimentally. Note that this lack of interaction on the time scale of the heterogeneous electron transfer to the electrode does not preclude rapid intramolecular electron transfers in the radical anions (at a frequency of 10^6 to 10^8 s^{-1}) as has been observed in related compounds [15].
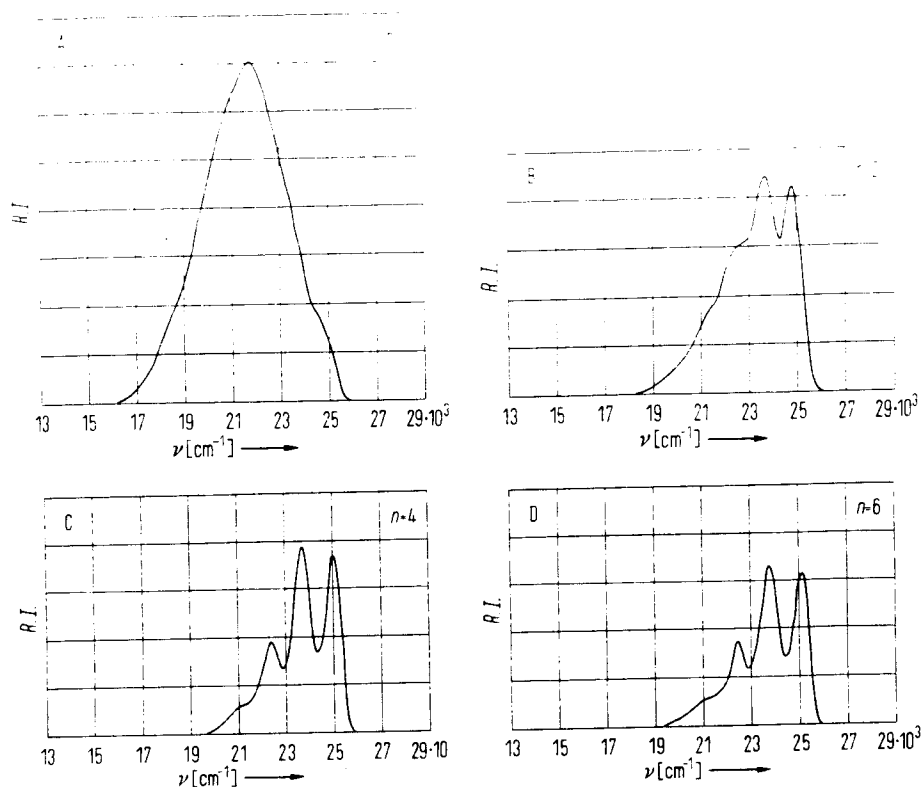
Fig. 2. Fluorescence spectra (corrected) at room temperature of α,ω-9,9'-dianthrylalkanes, with $n = 0, 2, 4, 6$, 2 to 3×10^{-5} M solutions in benzene-acetonitrile (1 : 1 by volume)

compounds described here occurs, the stability of the radical cations of dianthrylalkanes was too low the obtain ECL spectra without complications due to decomposition reactions. For example, the ECL observed for the $n = 2$ compound spectrum showed long wavelength bands of variable relative intensity similar to the ECL found with anthracene [31]. This instability of the radical cations also prevented a voltammetric study of the oxidation of these compounds. For ECL experiments instead of the generation of the radical cations of the parent molecules as oxidants, 10-methylphenothiazine (10-MP), which oxidized at 0.72 V vs. SCE, was employed. ECL was obtained for all of the compounds ($n = 0, 2, 4, 6$); the ECL spectra were almost identical to the fluorescence spectra of the dianthrylalkanes shown in Fig. 2. No enhancement of the intramolecular excimer band was observed even in the $n = 0$ and 2 compounds which show excimer bands in the fluorescence spectra.

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