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ELECTROORGANIC CHEMISTRY XVI

THE INTRAMOLECULAR NONBONDING INTERACTION BETWEEN TWO UNSATURATED SYSTEMS IN THE ANODIC ELECTRON TRANSFER PROCESS

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Generally, an intramolecular nonbonding interaction between two unsaturated systems has been observed in the hitherto known charge transfer process, such as the formation of a charge transfer complex from [2,2]paracyclophane and tetracyanoethylene[1]. However, the contribution of the similar nonbonding interaction to the generation of a cation radical by the anodic electron transfer from nonconjugated diene or related systems is not scrutinized as yet.

In the present study, the polarographic half-wave oxidation potentials ($E_{1/2}$) of 2-substituted norbornadiene (**1**), 2-substituted bicyclo[2,2,2]octadiene-2,5 (**2**) and some 4-substituted [2,2]paracyclophane (**3**) were measured to clarify the participation of the nonbonding interaction. Values of $E_{1/2}$ of these compounds (**1**,**2** and **3**) are shown in Table I. Fig.1 exhibits the plot of $E_{1/2}$ vs. σ_m and strongly

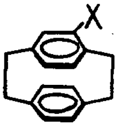
Table I. $E_{1/2}$ of **1**,**2** and **3**.

Substituent (X)	$E_{1/2}$[a)] V. vs. sce. **1**	**2**	**3**
a : H	1.54	1.82	1.47
b : CO_2Me			1.61
c : CO_2Et	1.85	2.11	
d : COMe	1.85	2.07	1.57
e : CN	1.99	2.22	1.65
f : NO_2			1.72

a) Studied with a three-electrode polarograph using a rotating platinum electrode in acetonitrile containing 0.1M lithium perchlorate.

1a,c,d,e

2a,c,d,e



3a,b,d,e,f

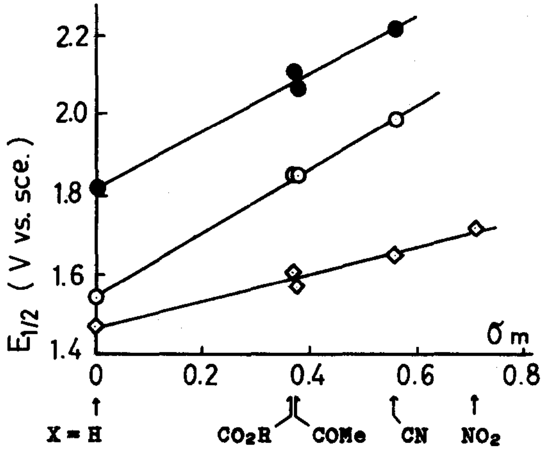


Fig.1 Plot of $E_{1/2}$ of **1** (○), **2** (●) and **3** (◇) vs. σ_m.

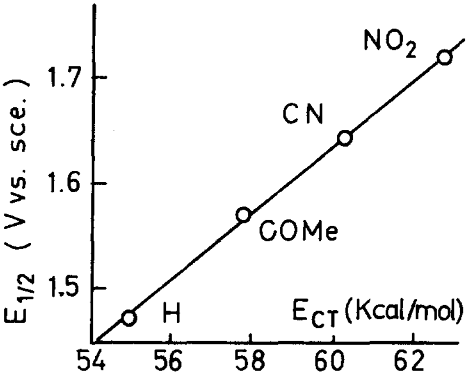


Fig.2 The relationship between $E_{1/2}$ of **3** and the charge transfer energy (E_{CT}) observed in the CT-complex formation from **3** and TCNE.

suggests the existence of the nonbonding interaction in the anodic electron transfer from the compound **1**,**2** or **3**, where the electron is removed from the unsaturated system not substituted with the electron withdrowing group.

According to the Traylor's notion[2], the charge transfer process may be classified into two categories, namely vertical and nonvertical processes. As shown in Fig.2, the remarkably good linear relationship between $E_{1/2}$ and E_{CT} of **3**[1] would convincingly demonstrate that the anodic electron transfer from [2,2]paracyclophane is a vertical process. On the other hand, the ionization potentials of a series of the 1-substituted 2-phenylcyclopropane (**4**) have been reported[2] to be independent to the substituent, whereas considerable dependence on the substituent was previously found in $E_{1/2}$ of **4**[3], implying the nonvertical nature of the anodic electron transfer from **4**. Thus, it could be suggested at the present stage that the anodic electron transfer from a rigid system such as [2,2]paracyclophane is a vertical process, whereas that from a certain non-rigid system is nonvertical.

Reference

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