Correlation of Reduction Potentials of Cyanine Dyes with their Orbital Energies

Jamil Ahmad and K. Brian Astin

Chemistry Department, University College, PO Box 1082, Manama, Bahrain

SUMMARY

The relationship between the reduction potential and calculated electron affinities of some thiacyanine dyes is examined. The results show that there is an excellent correlation between these two parameters of the dyes.

INTRODUCTION

The class of cyanine dyes represents an interesting series of substrates for experimental and theoretical study. Class members differ only in the numbers of conjugated double bonds, rendering them amenable to study by simple theoretical models. Theoretical results may then be correlated with experimental quantities such as ionisation energies measured by photo-electron spectroscopy (PES) (see e.g. Ref. 1), electron affinities obtained by electron transmission spectroscopy (ETS) (see e.g. Ref. 2) and electrochemi-cally determined reduction potentials (see e.g. Ref. 3).

In the present study we have carried out cyclic voltammetric experiments on a series of four thiacyanine dyes, hereafter referred to as Dye **0, 1, 2** or **3** corresponding to the value of x which is 0, 1, 2 or 3 respectively. The purpose of the study was to investigate the relationship between reduction potential

217
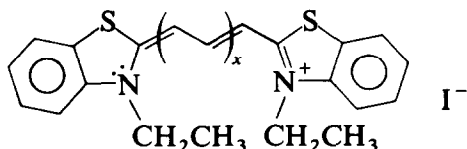
and quantum mechanically calculated electron affinities, using the particle-in-a-box, simple Hückel molecular orbital and MNDO (modified neglect of differential overlap)[4] methods. In the former two models, electron affinities are equated with the energy of the lowest unoccupied molecular orbital (LUMO) in accord with Koopmans's theorem.[5] With SCF methods the correlation between the first virtual orbital energy and electron affinity is often poorly described[6] so our MNDO results are calculated as zeroth order ionisation potentials, i.e. the ionisation potential of the singly occupied molecular orbital (SOMO) of the reduced species, producing electron affinities of a more realistic magnitude.

EXPERIMENTAL

The cyclic voltammograms were obtained using an approximately 10^{-4} M solution of each dye in propylene carbonate (PC) at 25°C, which had 1M-$LiClO_4$ as the background electrolyte, using a Metrohm 506 Polaricord with three-electrode system. The reference electrode was $Ag/AgCl/LiCl(CH_3CN)$ (satd). The auxiliary electrode was made of a platinum wire, and a glassy carbon working electrode was used. The voltammogram was traced on an $X-Y$ recorder. The dyes were obtained from K & K Labs, New York, USA, and used without further purification.

Nitrogen was bubbled through the solution for 10 min to remove oxygen prior to recording the voltammogram. The voltammogram was reversible in all the cases when PC was used as the solvent. With acetonitrile as the solvent, the return anodic peak disappeared, suggesting that the radical formed on reduction had reacted with the solvent or with water that is inevitably present in it.

RESULTS AND DISCUSSION

The cathodic and anodic peak potentials (E_{pc} and E_{pa}) were read from the voltammogram and their average taken to obtain the value of the half-wave potential, $E_{1/2}$. This half-curve potential corresponds to the thermodynamic redox potential, E^0, if the diffusion coefficients of the oxidised and reduced form are taken to be equal.

Figure 1 gives the voltammogram for Dye 3 in PC. The traces for the other dyes are similar. The fact that it is a one-electron reduction was ascertained from the values of the peak potentials using the formula which holds under the Nernst condition[7]

$$E_p \text{ (mV)} = \frac{56 \cdot 5}{n}$$
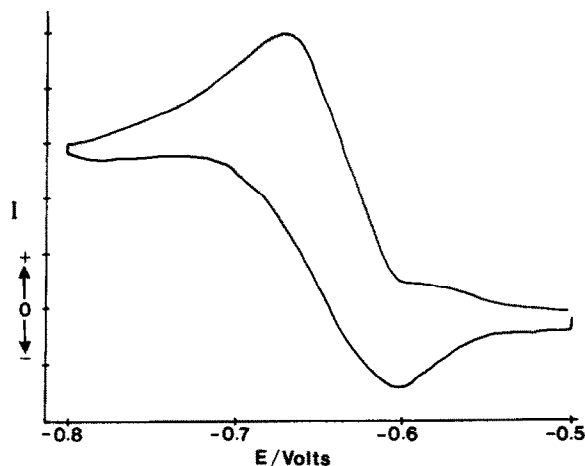
Fig. 1. Cyclic voltammogram of Dye 3 in PC at 25°C. Background electrolyte is 1M-LiClO$_4$, scan rate 10 mV s^{-1}.

where E_p is the difference in the anodic and cathodic peak potentials and n is the number of electrons.

Table 1 summarises the experimental $E_{1/2}$ values as well as the calculated values of the electron affinities using each of the approaches; the particle-in-a-box and the Hückel method reported by other workers[8] as well as the MNDO calculations carried out by us. The experimental results compare well with the polarographic values reported by Large.[9] However, the present study has established the reversibility and one-electron nature of the reduction. The values reported for the particle-in-a-box method had an error in that the box length (L in the well-known formula $E_n = n^2h^2/[8mL^2]$) was not correctly taken. The correct length should have been $(p + 2)l$ and not $(p + 3)l$, where p is the number of C atoms in the polyene chain and l is the

TABLE 1

Observed $E_{1/2}$ Values and Calculated Energies

Dye	$E_{1/2}$ (V)	E (particle-in-box) (eV)[a]	E (Hückel)-α/β[b]	E (MNDO) (eV)[c]
0, $x = 0$	-1.335	12.45	-0.609	-2.60
1, $x = 1$	-0.974	9.93	-0.448	-3.05
2, $x = 2$	-0.781	8.65	-0.353	-3.34
3, $x = 3$	-0.637	7.88	-0.276	-3.54

[a] Box length N–N distance + 1 bond length.[8]
[b] Ref. 8.
[c] Energy of SOMO in reduced species calculated by the half-electron method within MNDO approximation.[4]
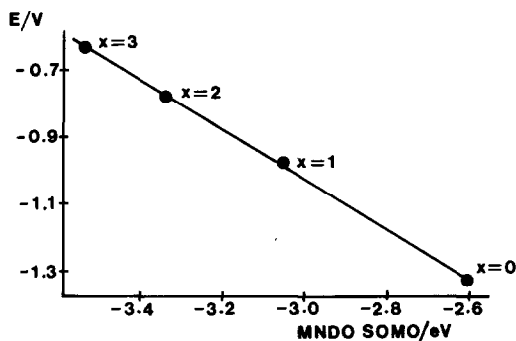
Fig. 2. $E_{1/2}$ (V) against SOMO (eV) for the series.

average bond distance in the chain. The box is assumed to extend half a bond-length beyond each nitrogen atom.

For the Hückel calculation the entire π-system was taken into account. Using the usual assumptions of the Hückel model, the secular matrix (which is 19×19 for Dye **0**) was set up and solved to get 19 energy states which were all non-degenerate. The 22 electrons in Dye **0** fill up 11 energy states, making $E(12)$ the LUMO. The value of LUMO is obtained in terms of α and β which are standard parameters for carbon.

The MNDO calculations were carried out on the polyene fragment of the dye to calculate the energy of SOMO (singly occupied molecular orbital) of the radical formed by the reduction of the cation, using the half-electron method.[10] All the bond lengths were optimised and the standard bond angles were assumed.

Excellent correlation is obtained between $E_{1/2}$ and the calculated energies by all methods. The linear least-squares correlation coefficients are better than 0·998 for all the methods; see for example Fig. 2.

REFERENCES

1. A. D. Baker, *Acc. Chem. Res.,* **3**, 17 (1970).
2. K. D. Jordan and P. D. Burrow, *Acc. Chem. Res.,* **11**, 341 (1978).
3. G. J. Hoijtink, *Rec. Trav. Chim. Pays-Bas,* **74**, 1525 (1955).
4. M. J. S. Dewar and W. Thiel, *J. Amer. Chem. Soc.,* **99**, 4899 (1977).
5. T. Koopmans, *Physica,* **1**, 104 (1933).
6. A. Szabo and N. S. Ostlund, *Modern quantum chemistry,* p. 194. Macmillan, New York (1982).
7. J. Heinze, *Angew. Chem. Int. Ed.,* **11**, 831 (1984).
8. J. F. Farrell, *J. Chem. Educ.,* **62**, 351 (1985).
9. T. H. James, ed., *The theory of the photographic process,* 4th edn, p. 203. Macmillan, New York (1977).
10. M. J. S. Dewar, J. A. Hashmall and C. G. Verrier, *J. Amer. Chem. Soc.,* **90**, 1953 (1968).