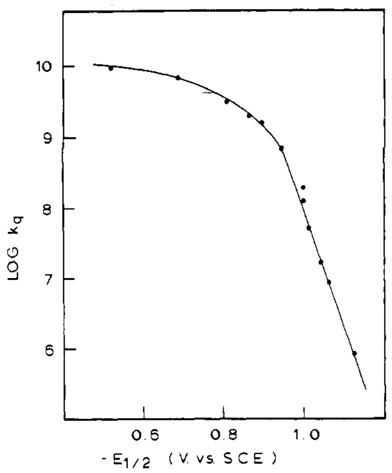

Figure 1. Plot of log k_q^{obsd} vs. quencher reduction potential, $E_{1/2}[Q/Q^-]$.

$k_{30}/2] = 10.6$. Although the exact value to be chosen here is uncertain, a value in the region 10.0–11.0 is clearly reasonable.[8] For the points in the linear portion of Figure 1, extrapolation of lines with limiting slopes to this region gives $E_{1/2}[\text{Ru(bipy)}_3^{3+}/\text{Ru(bipy)}_3^{2+*}] = -0.81 \pm 0.02$ V after correcting for w_p.[10] From the potential of the ground state $\text{Ru(bipy)}_3^{3+}/\text{Ru(bipy)}_3^{2+}$ couple in the same medium (+1.29 V),[12] it can be seen that excitation increases the reducing power of Ru(bipy)_3^{2+} by 2.10 V. Since the spectroscopically estimated excited state energy of Ru(bipy)_3^{2+*} is 2.18 V, essentially all of the excitation energy can be applied to driving the electron-transfer process. As expected,[8] this indicates that the entropy difference between the ground and excited states is small. We are currently extending our investigation to other metal complexes having long-lived excited states of different orbital origin.

Acknowledgment. The authors are grateful for support of this work by grants from the Army Research Office (DAHCO4 74 G 0025) and the National Science Foundation (GP42846X).

References and Notes

(1) H. D. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, **94**, 8238 (1972).
(2) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **95**, 5159 (1973).
(3) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974).
(4) G. Navon and N. Sutin, *Inorg. Chem.*, **13**, 2159 (1974).
(5) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2108 (1944).
(6) R. C. Jarnagin, *Acc. Chem. Res.*, **4**, 420 (1971).
(7) C. R. Bock, Ph.D. Dissertation, University of North Carolina, Chapel Hill, N.C., 1974.
(8) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969).
(9) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1974).
(10) w_p can be estimated from Debye-Hückel theory[11] as ca. −0.026 V in the present case and w_r (arising from ion dipole interactions) is assumed negligible.
(11) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer", Ronald Press, New York, N.Y., 1966.
(12) Gilbert M. Brown, Ph.D. Dissertation, University of North Carolina, Chapel Hill, N.C., 1974.

C. R. Bock, T. J. Meyer,* D. G. Whitten*
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514
Received December 4, 1974

Enantioselective Reduction in a Chiral Double Layer

Sir:

The double layer at an electrode-solution interface is known to influence the mechanisms of electrochemical reactions in two distinct ways. The relative concentrations of ions and solvent molecules in this region of solution can determine which intermolecular, secondary reaction paths are available to a reactive intermediate generated by electron transfer.[1-4] Also, serving as the reaction medium, the double layer may alter the activities of reactants and intermediates. This latter role, though more general than[5,6] the former is less well understood particularly in the case of the compact double layer, and its consequences have not been extensively explored. We wish to report a novel example of electrochemical selectivity which reflects the influence of the double layer as a reaction medium.

Table I. Cathodic Reduction of Co(acac)_3 at −1.0 V with 0.10 *M* Trimethyl-(−)-menthylammonium Perchlorate in Acetonitrile

$[\text{I} - \text{D}]_0 + [\text{I} - \text{L}]_0$ $M \times 10^3$	Conversion, %	Optical purity[8] (%) ± 0.06	k_d/k_l
4.10	46.5	1.02	1.033
4.62	81.7	2.30	1.028
7.82	50.1	1.23	1.036
16.28	75.4	1.87	1.027
31.28	61.2	1.38	1.030
			Mean 1.031 ± 0.003

The reduction of cobalt trisacetylacetonate, I, in acetonitrile, at a mercury cathode proceeds via an irreversible, one-electron, electrochemical-chemical process to yield the oligomeric Co(II) complexes $[\text{Co(acac)}_2]_n$, $n = 1$–4.[7] When the reaction was carried out using an optically active supporting electrolyte, tri-*N*-methyl-(−)-menthylammonium perchlorate, II, a small but reproducible enantioselectivity was observed. For example, racemic I was reduced at a controlled potential of −1.0 V vs. Ag|AgCl and the reaction stopped prior to complete conversion. The unreacted I was recovered and found to be optically active.[8] The optical purity increased with increasing conversion, obeying a pseudo-first-order rate law:

$$\text{I—D} \xrightarrow{k_d} \text{Co(acac)}_2 + \text{acac}^-$$

$$\text{I—L} \xrightarrow{k_l} \text{Co(acac)}_2 + \text{acac}^-$$

$$k_d/k_l = \frac{\ln (\text{I—D})/(\text{I—D})_0}{\ln (\text{I—L})/(\text{I—L})_0}$$

Table I shows the results of a representative series of experiments. The selectivity, k_d/k_l, is independent of the initial concentration of I and the extent of conversion. These apparent rate constants may, in principle, represent any one or a composite of the following elementary steps: (i) mass transport of I to the electrode surface, (ii) adsorption of I at the electrode, (iii) electron transfer, involving either "free" or adsorbed I.

Experimental conditions can control which of these steps will be rate limiting. In the experiments described here, the catholyte solution was efficiently stirred over a stationary electrode in a partitioned cell. Figure 1 shows the logarithm of the faradaic current[10] as a function of stirring rate and applied potential. At high overpotential ($E < -2.0$ V), the rate is purely mass-transport controlled as demonstrated by the insensitivity to potential and dependence on stirring rate.[11] At potentials above −1.1 V the rate becomes independent of stirring and above −1.0 V a simple exponential dependence on potential (Tafel relation) is observed; characteristic of rate limiting electron transfer (activation overpotential).[12]

The magnitude of the enantioselectivity varies systematically with potential and electrolyte concentration as shown in Figure 2. Two conclusions may be drawn from compari-

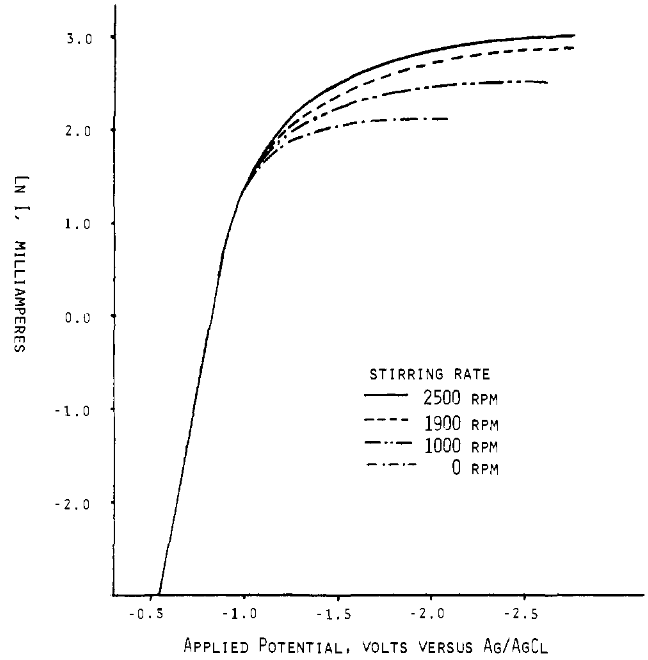

Figure 1. Pulse voltammetry of 0.001 M CO(acac)$_3$ in 0.1 M II-acetonitrile, at a 13-cm^2 Hg electrode.

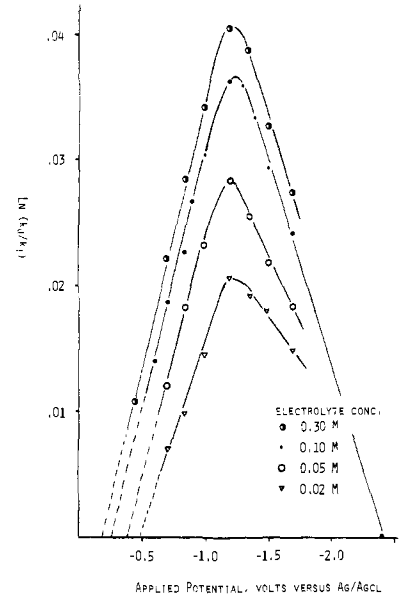

Figure 2. The effect of potential on enantioselectivity.

son of these data. (1) The decrease in selectivity at potentials between -1.20 and -2.4 V corresponds to measurements made under conditions of increasing mass-transport control. Thus, little or no selectivity is associated with mass transport. (2) In the region of pure activation overpotential, ($E > -1.0$ V), ln (k_d/k_l) increases linearly with decreasing potential. The selectivity must therefore be associated with a potential dependent process at the electrode surface.

Specific adsorption of I is apparently not involved. Zero-time extrapolation of coulometric transients[13] measured with and without I were found to be the same within experimental error. We conclude that electron transfer per se, under the influence of the chiral double layer, is the selective process.

Several authors have provided quantitative models for the influence of double layer on electrode kinetics.[14-16] In these treatments, only average electrostatic interactions are included. Since enantioselectivity reflects a discrimination based purely on substrate structure, it must be concluded that interactions with the double layer also have a significant steric component.

Included in Figure 2 is the effect of electrolyte concentration. It was found that, for each concentration, the X intercept at low overpotential corresponded to the potential of zero charge excess (pzc).[19] Since the surface concentration of cations at the pzc cannot be less than their concentration in the bulk solution, it is noteworthy that no selectivity exists at this potential regardless of the electrolyte concentration. It may be inferred that some factor other than the mere presence of asymmetric cations is required for selectivity. We propose that this factor is the orientational ordering of electrolyte dipoles in the Helmholtz plane.[17] An interfacial potential gradient, capable of imposing such order, would be lacking at the pzc but may be quite substantial at other applied potentials.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Du Pont De Nemours and Co. for a young Faculty Grant, for the support of this work.

References and Notes

(1) M. M. Baizer, *J. Electrochem. Soc.*, **11**, 215 (1964).
(2) R. Galli and F. Olivani, *J. Electroanal. Chem.*, **25**, 331 (1970).
(3) R. Breslow and R. F. Drury, *J. Am. Chem. Soc.*, **96**, 4702 (1974).
(4) L. Horner and D. Degner, *Tetrahedron Lett.*, 5889 (1968); L. Horner and D. H. Skaletz, *ibid.*, 3679 (1970); L. Horner and R. Schneider, *ibid.*, 3133 (1973); L. Eberson and L. Horner in "Organic Electrochemistry", M. M. Baizer, Ed., Marcel Dekker, New York, N.Y., 1973 pp 869–893; R. N. Gourley, J. Grimshaw, and P. G. Millar, *Chem. Commun.*, 5889 (1971); E. Kariv et al., *Electrochim. Acta*, **18**, 433 (1973); M. Jubault et al. *C. R. Acad. Sci., Ser. C*, **277**, 583 (1973).
(5) P. Delahay, "Double Layer and Electrode Kinetics", Wiley, Interscience, New York, N.Y., 1965.
(6) R. W. Murray and M. Kodama, *Anal. Chem.*, **37**, 1759 (1965).
(7) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, I (1964); F. A. Cotton and R. C. Elder, *ibid.*, **4**, 1145 (1965).
(8) Control experiments established that the observed rotations were not artifacts of the work-up or analysis. Moreover, when an achiral electrolyte, tetra-*n*-butylammonium perchlorate, was employed, no selectivity could be detected. Optical purities were calculated assuming a molecular rotation of 29,700° at 546 mμ for optically pure I.[9]
(9) J.-Y. Sun, Ph.D. Thesis, University of North Carolina, 1967.
(10) Currents were sampled at 200 msec following the application of a given potential.
(11) The hydrodynamics of turbulent flow (B. G. Levich, "Physicochemical Hydrodynamics", Prentice-Hall, Englewood Cliffs, N.J., 1962, Chapter 3) are probably applicable although the dependence on stirring rate (roughly $\omega^{1/3}$) cannot be simply derived.
(12) J. P. Brenet, K. Traore "Transfer Coefficients in Electrochemical Kinetics", Academic Press, New York, N.Y., 1971.
(13) J. H. Christie, R. A. Osteryoung, and F. C. Anson, *J. Electroanal. Chem.*, **13**, 236 (1967).
(14) A. N. Frumkin, *Z. Phys. Chem.. Abt. A*, **164**, 121 (1933).
(15) W. H. Reinmuth, L. B. Rogers, and L. E. I. Hummelstedt, *J. Am. Chem. Soc.*, **81**, 2947 (1959).
(16) M. Breiter, M. Kleinerman, and P. Delahay, *J. Am. Chem. Soc.*, **80**, 5111 (1958).
(17) Evidence for crystalline order of an adsorbed electrolyte has been described: C. M. Elliot and R. W. Murray, *J. Am. Chem. Soc.*, **96**, 3321 (1974).
(18) On leave from the Department of Synthetic Chemistry, Kumamoto University, Kumamoto, Japan.
(19) Measured by mercury drop extrusion: F. C. Anson, *Anal. Chem.*, **38**, 54 (1966).

Stephen Mazur,* Katsutoshi Ohkubo[18]
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

Received December 20, 1974

Reaction of Ketone Enolates with Copper Dichloride. A Synthesis of 1,4-Diketones

Sir:

Copper-promoted dimerization of carbanions has constituted a convenient method of carbon–carbon bond forma-