Johnson, and H. Beinert, *Proc. Nat. Acad. Sci. U.S.A.*, **66**, 1157 (1970).

(6) J. P. Collman, T. N. Sorrell, and B. M. Hoffman, *J. Am. Chem. Soc.*, **97**, 913 (1975).

(7) S. Koch, S. C. Tang, R. H. Holm, R. B. Frankel, and J. A. Ibers, *J. Am. Chem. Soc.*, **97**, 916 (1975).

(8) P. K. Warme and L. P. Hager, *Biochemistry*, **9**, 1606 (1970).

(9) T. G. Traylor and C. K. Chang, unpublished results.

(10) J. O. Stern and J. Peisach, *J. Biol. Chem.*, **249**, 7495 (1974).

(11) The fractions of the Soret peaks were estimated by comparison with spectra of CO–Fe(II) porphyrins of equivalent total heme concentration (see ref 10). The fractions of the longer wavelength absorption peaks given here are the upper limits that could be maximized with the NMe_4OH base.

(12) Neither the nonpolar, polar (DMF, HMPA), nor protic (alcohol, aqueous detergents suspensions) solvents were successful.

(13) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).

(14) C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, **96**, 2250 (1974).

(15) Dibenzo-18-crown-6 was prepared according to: C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967). It was purified by vacuum distillation before use.

(16) W. S. Brinigar and C. K. Chang, *J. Am. Chem. Soc.*, **96**, 5595 (1974).

(17) Determined by the Evans method, using DMSO as solvent.

(18) C. K. Chang and T. G. Traylor, *J. Am. Chem. Soc.*, **95**, 8475 (1973).

(19) A. Nakahara and J. H. Wang, *J. Am. Chem. Soc.*, **80**, 6526 (1958).

(20) C. K. Chang and T. G. Traylor, *Biochem. Biophys. Res. Commun.*, **62**, 729 (1975).

(21) When the species c was allowed to stand at room temperature under 1 atm of O_2 for longer period of time, it lost reversibility toward CO binding and was presumably oxidized to an Fe(III) species. The spectrum (curve c) also changed with time.

(22) The 412-nm Soret peak appeared when the *n*-BuOH content was higher than 20%. Nonpolar solvents were tried but results were inconclusive since mercaptide salt was precipitated.

(23) J. T. Snow, J. W. Finley, and M. Friedman, *Biochem. Biophys. Res. Commun.*, **64**, 441 (1975).

(24) Since the receipt of this manuscript J. P. Collman and T. N. Sorrell *J. Am. Chem. Soc.*, **97**, 4133 (1975), have reported similar spectral changes in benzene using crown ether complexes of alkyl mercaptides. These observations also exclude the binding of DMSO.

C. K. Chang, D. Dolphin*

Department of Chemistry, The University of British Columbia
Vancouver, British Columbia, Canada V6T 1W5

Received July 5, 1975

Aromatic Hydrocarbon–Diene Exciplexes. The Importance of Reversible Exciplex Formation

Sir:

The interaction of aromatic hydrocarbon excited singlet states with ground state dienes and olefins has attracted considerable interest in the past decade.[1-8] The initial observation of fluorescence quenching by Hammond and coworkers[1a] and subsequent observations of long-wavelength emission[3,4] and cycloaddition[5-8] have been attributed to the formation of an exciplex intermediate (eq 1).[1-9]

$$\begin{array}{ccccc} & & & \overset{k_n}{\nearrow} & A + D \\ A^* + D & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & (AD)^* & \xrightarrow{k_r} & A + D + h\nu' \\ & & & \underset{k_a}{\searrow} & \text{adducts} \end{array} \qquad (1)$$

Rate constants for fluorescence quenching generally decrease with increasing diene ionization potential, as shown in Figure 1 for quenching of naphthalene[1a] and *trans*-stilbene. Evans[2] attributed the variation in rate constant with ionization potential to a charge-transfer mechanism for exciplex formation. The free energy change for electron transfer as given in eq 2[2,10] correctly predicts a linear relation-

$$\Delta G_{\mathrm{ET}} \propto \text{ionization potential (D)} - \text{electron affinity (A*)} \qquad (2)$$

ship between log k_q and diene ionization potential for endothermic electron transfer. An electron-transfer mechanism does not satisfactorily explain (a) the large variation in excited aromatic sensitivity to diene ionization potential (slopes in Figure 1), (b) the absence of significant rate enhancement by polar solvents,[1c] and (c) the anomalously rapid quenching rates of cyclic dienes for some aromatic hydrocarbons (e.g., naphthalene, anthracene)[1b,c] but not for others (e.g., *trans*-stilbene, phenanthrene).

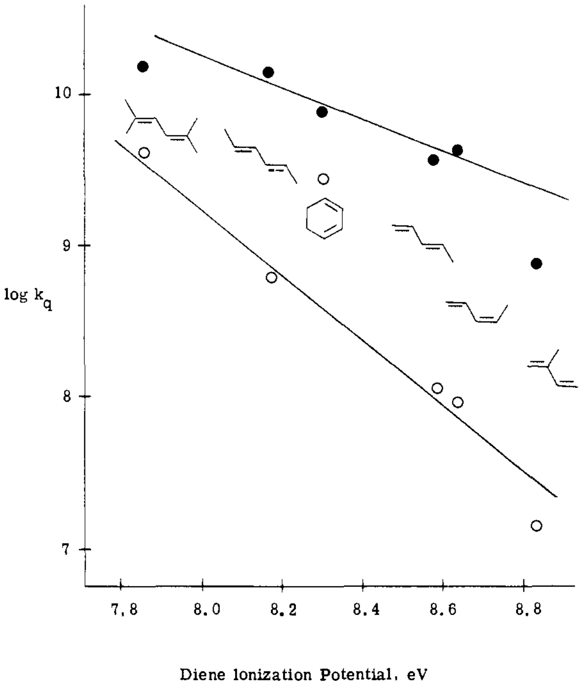

Figure 1. Correlation of quenching rate constants for *trans*-stilbene (●) and naphthalene (○)[1a] with diene vertical ionization potential.[1b]

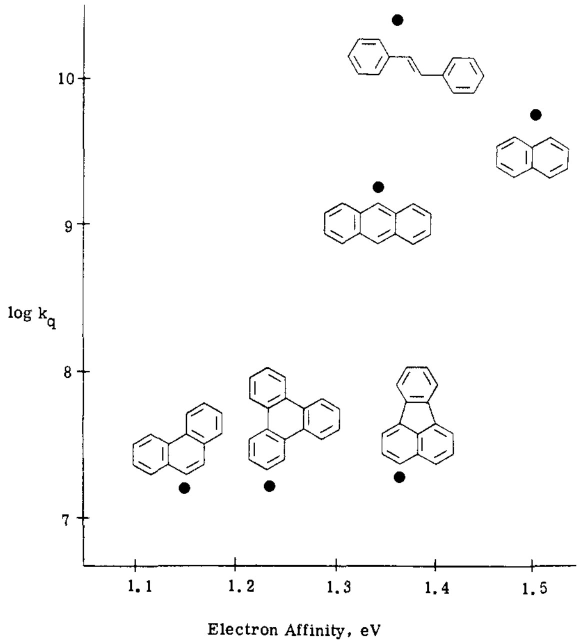

Figure 2. Correlation of 2,5-dimethyl-2,4-hexadiene quenching rate constants with excited state electron affinities.

For the interaction of a series of excited aromatic hydrocarbons with a single diene, it should be possible to correlate quenching rate constants with excited state electron affinity (eq 2).[10] Our attempts at such a correlation are shown in Figure 2. Even allowing for the large errors involved in estimating electron affinities[10] from singlet energies[11] and ground state reduction potentials,[12] the results proved less than gratifying. However, the recent kinetic analysis of α-cyanonaphthalene olefin exciplexes by Ware[13] indicates that reversible exciplex formation can lead to ob-

Table I. Arrhenius Parameters for Quenching of Aromatic Hydrocarbon by 2,5-Dimethyl-2,4-hexadiene

Fluorescer (A*)	Electron affinity, eV[a]	10^8k_q, M^{-1} sec^{-1} (23°C)[b]	$\Delta E^{\ddagger}$,[c] kcal	$\Delta S^{\ddagger}$, eu
Naphthalene	1.51	28	0.52	−16
		0.93[d]	−1.5[d]	
trans-Stilbene	1.37	160	3.3	−1
Anthracene	1.35	13	−2.8	
Fluoranthene	1.37	0.16	−7.4	
Triphenylene	1.24	0.15	1.5	−24
Phenanthrene	1.15	0.14	1.8	−22

[a] $-E_S - E_{1/2}(A/A^-)$, see text. [b] Obtained from the slope of linear Stern–Volmer plots for fluorescence intensity and/or lifetime quenching in degassed benzene solution. Singlet lifetimes measured by single-photon counting except for *trans*-stilbene ($\tau \sim 2 \times 10^{-10}$ sec[5b]). [c] Obtained from slope of plots of log (k_q) vs. T^{-1}, minimum of six temperatures between 5 and 75°C. Corrected for the variation in fluorescer singlet lifetime and solvent density with temperature. [d] Quenching by *cis*-1,3-pentadiene.

served fluorescence quenching rates (k_q) significantly slower than the rate of exciplex formation (eq 3, $k_p = k_n + k_r + k_a$). This report prompted us to examine the temperature

$$k_q = k_1(k_p)/(k_p + k_{-1}) \tag{3}$$

dependence of the rate constants for quenching of aromatic hydrocarbon fluorescence by dienes.[14]

Arrhenius parameters for fluorescence quenching by 2,5-dimethyl-2,4-hexadiene are given in Table I. Values for *trans*-stilbene are consistent with diffusion-controlled, irreversible quenching.[13] Values of $\Delta E^{\ddagger}$ for all of the other aromatic hydrocarbons are smaller than 2 kcal/mol, negative temperature coefficients being observed for anthracene and fluoranthene. Negative temperature dependence is a consequence of a substantially more positive $\Delta S^{\ddagger}$ for exciplex dissociation (k_{-1}) than for exciplex reactions (k_p). Unfortunately, the individual rate constants in eq 3 cannot be separated due to the absence of exciplex emission.[13] However, it appears likely that the large variation in room temperature fluorescence quenching rate constants for *trans*-stilbene, anthracene, and fluoranthene (Figure 2) is the consequence of increasing exciplex reversibility rather than decreasing rates of exciplex formation.

Once the reversible nature of aromatic hydrocarbon–diene exciplex formation is recognized, the previously mentioned problems of interpreting exciplex kinetics can be readily explained. The decrease in fluorescence quenching rate constants with diene ionization potential (Figure 1) reflects increased reversibility of exciplex formation and not simply a decrease in the rate constant for exciplex formation.[2] Quenching of naphthalene by 2,5-dimethyl-2,4-hexadiene (IP = 7.84[1b]) displays a small positive temperature dependence, whereas quenching by *cis*-1,3-pentadiene (IP = 8.65[1b]) displays a negative temperature dependence. Reversible exciplex formation becomes increasingly important with less electron-rich dienes.[13] The absence of large kinetic solvent effects is also explicable in terms of reversible exciplex formation. Even if charge resonance stabilization is responsible for exciplex formation, no simple solvent dependence would be expected for the complex quenching rate constant (eq 3). Finally, the enhanced quenching of naphthalene and anthracene by cyclohexadiene vs. acyclic dienes[1b,c] may also be a consequence of reversible exciplex formation. Yang[6] has reported high quantum yields for 4 + 4 cycloadduct formation from naphthalene and anthracene with cyclohexadiene. If k_a (and hence k_p) is larger for cyclic vs. acyclic dienes with similar values of k_1 and k_{-1}, then enhanced quenching rates will be observed. Larger values of k_a would be expected for cyclic vs. acyclic dienes on the basis of increased frontier orbital overlap.[6b,7b,15] For *trans*-stilbene (Figure 1), triphenylene, and phenanthrene, frontier orbital overlap is comparable for cyclic and acyclic dienes, and enhanced quenching rate constants are not observed for cyclic dienes.

We conclude with a caveat concerning the interpretation of fluorescence quenching data obtained at a single temperature.[1-3,9] When quenching occurs via reversible exciplex formation, the observed quenching constants can be substantially lower than the rate constant for exciplex formation (eq 3). Changes in fluorescer and quencher structure can potentially alter all of the rate constants involved in exciplex formation and decay (eq 1).

Acknowledgment. Support of this work by the National Science Foundation (MPS 75-07181) is gratefully acknowledged.

References and Notes

(1) (a) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 126 (1968); (b) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Am. Chem. Soc.*, **94**, 3679 (1972); (c) G. N. Taylor and G. S. Hammond, *ibid.*, **94**, 3684 (1972).

(2) T. R. Evans, *J. Am. Chem. Soc.*, **93**, 2081 (1971).

(3) G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).

(4) N. C. Yang, International Exciplex Conference, London, Ontario, May 1974.

(5) (a) O. L. Chapman and R. D. Lura, *J. Am. Chem. Soc.*, **92**, 6352 (1970); (b) J. Saltiel, J. T. D'Agostino, O. L. Chapman, and R. D. Lura, *ibid.*, **93**, 2804 (1971).

(6) (a) N. C. Yang and J. Libman, *J. Am. Chem. Soc.*, **94**, 1405 (1972); (b) N. C. Yang, J. Libman, and M. F. Savitzky, *ibid.*, **94**, 9226 (1972).

(7) (a) F. D. Lewis and R. H. Hirsch, *Tetrahedron Lett.*, 4947 (1973); (b) F. D. Lewis, C. E. Hoyle, and D. E. Johnson, *J. Am. Chem. Soc.*, **97**, 3267 (1975).

(8) For a review of exciplex reactions see A. Lablache-Combier, *Bull Chim. Soc. Fr.*, 4792 (1972).

(9) (a) S. L. Murov, L. Yu, and L. P. Giering, *J. Am. Chem. Soc.*, **95**, 4329 (1973); (b) P. M. Froehlich and H. A. Morrison, *ibid.*, **96**, 332 (1974); (c) R. G. Brown and D. Phillips, *ibid.*, **96**, 4784 (1974).

(10) (a) D. Rehm and A. Weller, *Isr. J. Chem.*, 8, 259 (1970); (b) J. B. Guttenplan and S. G. Cohen, *Tetrahedron Lett.*, 2163 (1972).

(11) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, N.Y., 1971.

(12) G. Briegleb, *Angew. Chem.*, **3**, 617 (1964).

(13) W. R. Ware, D. Watt, and J. D. Holmes, *J. Am. Chem. Soc.*, **96**, 7853 (1974).

(14) Chapman and Saltiel[5] reported an inverse temperature dependence for the cycloaddition of *trans*-stilbene singlet with olefins; however, this evidence for reversible exciplex formation appears to have gone largely unnoticed.

(15) K. Fukui, *Fortschr. Chem. Forsch.* 15, 1 (1970).

(16) (a) Camille and Henry Dreyfus Teacher-Scholar; (b) Northwestern University Fellow.

Frederick D. Lewis,[16a]* **Charles E. Hoyle**[16b]
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received May 23, 1975

Electrochemical Generation of Stable Arene Metal Tricarbonyl Dianions

Sir:

Although a few reports have appeared in the literature regarding the nonaqueous electrochemical reduction of benzenetricarbonylchromium compounds, no detailed study has appeared regarding the reductive electrochemical characteristics of arene chromium carbonyl complexes.[1-4] Gubin has reported that the polarographic reduction of acetophenonetricarbonylchromium occurs by an electrode reversible one-electron process.[3,4] In contrast, Dessy et al.[1] report transferring two electrons per molecule of benzenetricarbonylchromium during an exhaustive controlled potential reduction. The resulting solution was oxidized to regenerate benzenetricarbonylchromium. In this paper, we wish to report our electrochemical studies on a variety of arene chromium carbonyl complexes in nonaqueous media and the