(14) For prismane literature see T. J. Katz and N. C. Acton, *J. Amer. Chem. Soc.*, **95**, 2738 (1974).

(15) NOTE ADDED IN PROOF. (a) We have recently obtained 1 with a $[\alpha]^{20}{}_{405}$ of $-136.7°$ (c 0.3 in abs. alcohol). (b) The conversion of **4** to **5** proceeds as shown in Scheme I in high yield. Positional isomers of the diphenyl **5** have not yet been detected.

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On the Mechanism of the Electrochemical Reduction of Cyclooctatetraene

Sir:

It has been known for some time that the ultimate product of the electrochemical reduction of cyclooctatetraene (COT) is a mixture of 1,3,5- and 1,3,6-cyclooctatriene.[1] However, the mechanism of this reduction has not been definitely elucidated. In particular it is not clear whether the eec (eq 1) or ece (eq 2) mechanism predominates in aprotic solvents containing tetraalkylammonium salts, other than methyl, as supporting electrolyte. In dimethylformamide

$$\mathrm{COT} \overset{e^-}{\rightleftarrows} \mathrm{COT}\cdot^- \overset{e^-}{\rightleftarrows} \mathrm{COT}^{=} \xrightarrow{H^+} \mathrm{HCOT}^- \xrightarrow{H^+} \mathrm{H_2COT} \qquad (1)$$

$$\mathrm{COT} \overset{e^-}{\rightleftarrows} \mathrm{COT}\cdot^- \xrightarrow{H^+} \mathrm{HCOT}\cdot \overset{e^-}{\rightleftarrows} \mathrm{HCOT}^- \xrightarrow{H^+} \mathrm{H_2COT} \qquad (2)$$

(DMF),[2] dimethyl sulfoxide (DMSO),[2] acetonitrile (MeCN),[3] tetrahydrofuran (THF),[3] and hexamethylphosphoramide (HMPA) solutions containing the tetra-*n*-propyl- or -butylammonium ion $(\mathrm{TBA})^+$ in the supporting electrolyte, two distinct one-electron reduction waves are observed polarographically at approximately -1.65 and -1.95 V *vs.* an aqueous saturated calomel electrode.[4] The eec mechanism was originally proposed by Allendoerfer and Rieger[2] to explain the two observed electrochemical steps and is supported by the known stability of $\mathrm{COT}\cdot^-$ in these solvents as demonstrated by esr and by the consistency of the AC polarographic rate data,[2,5] with this mechanism. The ece mechanism was proposed by Theilen and Anderson[3] where the first proton source is the quaternary ammonium ion and is supported by the observation that only one polarographic reduction wave is observed when this proton source is removed by substituting the tetramethyl ammonium ion (TMA^+) in the supporting electrolyte for TBA^+.

The correct mechanism for the reduction can be determined by simultaneous electrochemical electron spin resonance (SEESR).[6] Using this technique the esr signal intensity from $\mathrm{COT}\cdot^-$ can be monitored during a cyclic potential scan. It was shown[6] that for a diamagnetic → paramagnetic reduction where the product was stable, the esr–voltage curve closely resembled the integral of the current–voltage curve, *i.e.*, resembled a charge–voltage curve where increasing negative charge corresponds to an increase in esr signal.

Figure 1 shows, in the upper most curve, a standard cyclic voltammogram of 10^{-3} *M* COT in HMPA using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte on a hanging mercury drop electrode. The voltage sweep rate was 150 mV/sec. The sweep rate dependence of the curve is identical in every respect with that reported previously for DMF, TPAP solutions[2] except that the second reduction product is stable so its reoxidation may be observed even on slow scans. The central curve is a cyclic voltammogram recorded for the same solution at the same scan rate in our SEESR cell on a 15-cm^2 amalgamated gold electrode. The construction details of this cell will be described elsewhere.[7] For the experiments described herein, it performs identically with that previously described by Goldberg and Bard.[6] The lower most curve shows the intensity of the esr signal of $\mathrm{COT}\cdot^-$ as a function of voltage, recorded simultaneously with the current–voltage curve. The magnetic field of the esr spectrometer was adjusted to sit on a first derivative peak of the central line of the $\mathrm{COT}\cdot^-$ nonet throughout the experiment. No other esr spectra are observed by continuous electrolysis at any potential, so the esr signal intensity plotted is entirely due to $\mathrm{COT}\cdot^-$.

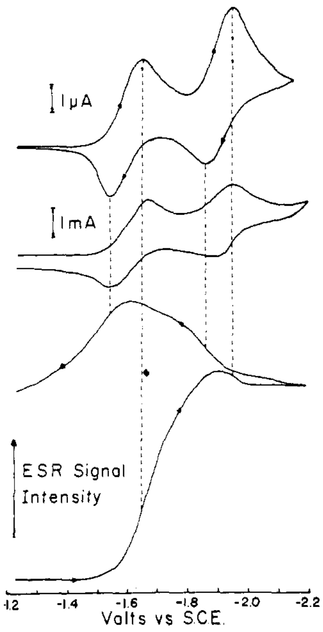

Figure 1. (Uppermost curve) Cyclic voltammogram of COT in HMPA on hanging mercury drop electrode. (Central curve) Cyclic voltammogram of same solution on 15 cm^2 amalgamated gold electrode in SEESR cell. (Lowermost curve) Esr-voltage curve recorded simultaneously with the voltammogram in SEESR cell.

This esr–voltage curve is identical with that shown by Goldberg and Bard[6] for two separate reversible one-electron reductions uncomplicated by following chemical reactions and thus confirms the eec hypothesis. Under the ece mechanism, the steady state concentration of $\mathrm{COT}\cdot^-$ would be determined by the rate of its production relative to the rate of its reaction with the proton donor so the esr signal intensity would be expected to follow the current–voltage curve at first and go through a maximum at the first cathodic peak potential. Thereafter, it should decrease monotonically as diffusion limits the amount of $\mathrm{COT}\cdot^-$ produced. Since the esr signal clearly does not decrease until a potential corresponding to the second reduction peak, $\mathrm{COT}\cdot^-$ must be stable until it becomes the electroactive species at the second peak in accordance with the eec mechanism. The subsequent sharp increase in the esr signal when the potential is again swept anodic of the second peak indicates the $\mathrm{COT}\cdot^- + e^- \rightleftarrows \mathrm{COT}^{2-}$ reaction is reversible.

Thus I have shown, contrary to the suggestion of Theilen and Anderson,[3] that the COT radical anion is stable in the presence of TBAP and can be reversibly reduced electrochemically to the dianion. Since the single dc polarographic reduction wave of COT in the presence of TMA^+ discussed by Theilen and Anderson[3] in MeCN solution and confirmed by Hayes, *et al.*,[8] for DMF solutions can no longer be explained in terms of the irreducibility of $\mathrm{COT}\cdot^-$, another explanation must be sought which will presumably involve specific ion pairing or chemical reactions between TMA^+ and $COT\cdot^-$.

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References and Notes

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Solvent Regulation of the Photoredox Behavior of Bromopentaamminecobalt(III) and Consequent Restrictions on the Possible Inferences from "Sensitized" Photoredox Reactions[1]

Sir:

Studies of "sensitized" photoredox reactions of coordination complexes have proved to be equivocal and controversial, being potentially complicated by radical reactions[2] and excited state electron transfer[3] reactions in addition to the more customary problems of donor instability. Thus, compelling evidence for excited state electron transfer from $Ru(bipy)_3^{2+}$ has been obtained with cobalt(III) complexes,[4] $Ru(NH_3)_6^{3+}$,[4,5] Fe^{3+} [5] among the relevant acceptors. The original impetus for study of "sensitized" photoredox reactions was the premise, borrowed in large part from mechanistic photochemical studies of organic systems,[6] that sensitized photoreactions could provide definitive information about excited state reactivity. For example, comparison of "sensitized" and direct photolysis photoredox yields has been the basis for determination of the efficiency of intersystem crossing between excited states of different spin multiplicity in $Co(NH_3)_6^{3+}$ [7] and $Co(HEDTA)X^-$ [2c] (X = Cl, Br, NO_2). More fundamentally, this mechanistic approach assumes that well-defined "molecular" excited states generated in an energy transfer process can be simply related to "molecular" excited states populated by direct excitation. We have now found that the environmental influence on the photoredox chemistry of $Co^{III}(NH_3)_5X$ complexes is so great that we must question the assumed "molecularity" of charge transfer to metal excited states; as a result it is in principle unlikely that sensitized and direct photolyses can be simply related.

Consideration of the implications of proposed photoredox models[8-10] has very recently led to investigations of photoredox processes of cobalt complexes in other than aqueous media.[11,12] The results of such investigations indicate that quantum yields for these photoredox processes are strongly medium dependent, often in varying with composition of the medium in very complex ways.[13] Of more specific significance to attempts to study sensitized photoredox reactions, the results now available for $Co(NH_3)_5NO_2^{2+}$,[11] for $Co(NH_3)_5NCS^{2+}$, [12] and reported here for $Co(NH_3)_5Br^{2+}$ (Figure 1) demonstrate that it is not possible to identify experimentally a quantum yield which can be uniquely associated with the redox decompositions of charge transfer excited states of these systems. At one extreme, the behavior of $Co(NH_3)_5NO_2^{2+}$ seems to approach expectation for limiting photodissociative charge transfer processes,[8-10] with the observed product yields a complex function of the dynamics of radical recombination and dissociation processes.[14] The behavior of other $Co(NH_3)_5X^{2+}$ (at least for X = NCS, N_3, Cl, and Br) is far more complicated and none of these four complexes appears to exhibit limiting photodissociative behavior in aqueous solution.[10b] Very striking qualitative variations in photoredox behavior have been found for $Co(NH_3)_5Br^{2+}$. This complex appears to approach photodissociative behavior in 80% acetonitrile-water solutions[15] and to be nearly photoinert in 87% phosphoric acid solutions (Figure 1). Furthermore, while a well-defined maximum photoredox yield can be established experimentally in aqueous and phosphoric acid media, photolyses in several other media have not been found to approach a defined maximum limiting value at high excitation energies. The major points with regard to the possibility of a meaningful study of sensitized photoredox reactions are (1) the qualitative nature of the photoredox process (*i.e.*, whether excited states can be regarded as "dossociative" or "bound") apparently depends on the solvent environment and (2) it is not possible to associate an intrinsic molecular quantum yield with the photoredox processes stimulated by direct CT excitation. Since the proximity of an excited state donor must constitute a major change in the nature of the solvent environment of an acceptor cobalt complex, we can see no hope of relating a sensitized photoredox quantum yield to

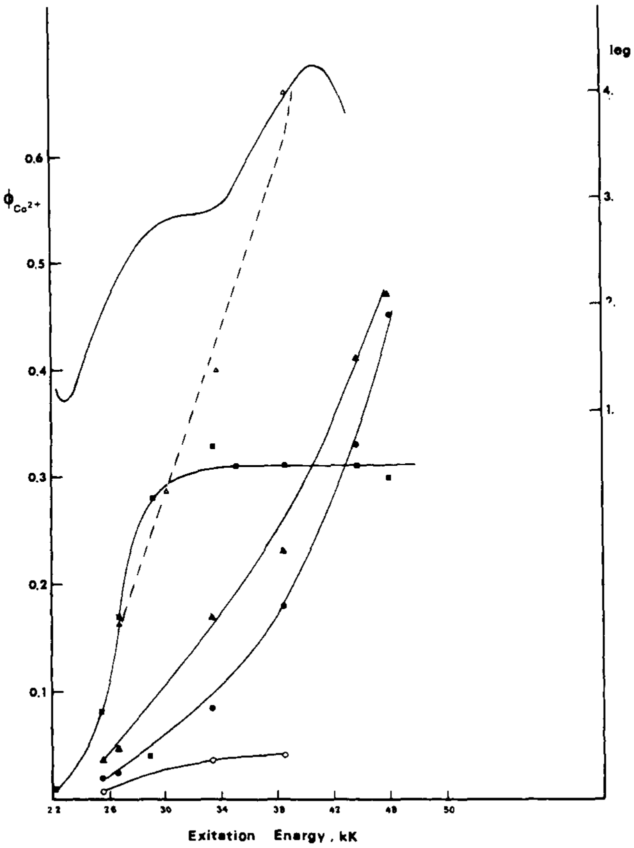

Figure 1. Absorption spectrum (upper curve, in water) and variations in the quantum yields of Co^{2+} (lower curves) with excitation energy and solvent medium obtained for irradiations of $Co(NH_3)_5Br^{2+}$. Aqueous solvent media employed: H_2O, ■; 80% CH_3CN, △; 50% glycerol, ▲; 75% glycerol, ●; 87% phosphoric acid, ○. Except for studies in phosphoric acid, all solutions were 10^{-3} *M* in $HClO_4$.