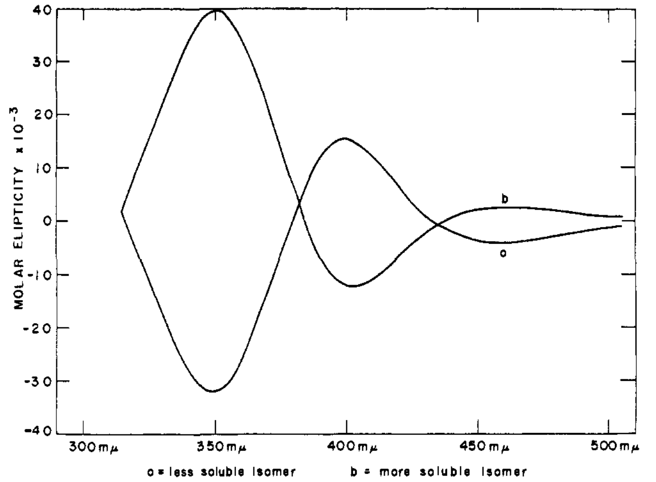

Figure 1. Circular dichroism spectra of the diastereomers of $[(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{C((S)\text{-}NHCHMePh)Me\}][BF_4]$.

$NaBH_4$ in ethanol gives two products in approximately equal amounts. One of these, **4**, is that expected from hydride attack at the carboxonium carbon; the other is the σ-ethyl $(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_2H_5)$ (**6**). These two complexes can be separated easily, **6** being considerably less soluble in hexane.[7] The reaction of **1** with $NaBD_4$ in EtOH gives $(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{CD(OEt)CH_3\}$ (**4a**) and $(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CD_2CH_3)$ (**6a**) which shows that all of the added hydrogens in the formation of **4** and **6** arise from the borohydride. The formation of **6** is difficult to explain; it has been found that **4** does not react with B_2H_6 or B_2H_6–$NaBH_4$ mixtures in EtOH; however, $[Ph(COEt)NEt_2][BF_4]$ reacts[8] with $NaBH_4$ to give $PhCH_2NEt_2$ which again supports the contention that **1** behaves as a carboxonium salt. We have synthesized **6** by an independent route: $(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$ was treated with $AgBF_4$ and ethylene to give $[(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)(h^2\text{-}C_2H_4)]BF_4$ (**7**); reduction of the latter with $NaBH_4$ yields **6**.

Primary amines and ammonia, but not secondary amines, react with **1** to give carbimonium salts; *e.g.*, (*S*)-(−)-α-phenylethylamine ($[\alpha]^{25}D$ −39.6°) gives a mixture of the diastereomers $[(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{C((S)\text{-}NHCHMePh)Me\}]BF_4$ (**8a** and **8b**). Resolution of the *RS* and *SS* isomers was achieved by fractionation from ethanol. As with **4**, the separation can be conveniently followed by nmr in the methyl region: nmr (δ in acetone-d_6) less soluble isomer (mp 195° dec) 1.61 (3, doublet, J = 6.8 Hz, CHMe), 2.85 (3, singlet, CMe); more soluble isomer (mp 186° dec) 1.44 (3, doublet, J = 6.8 Hz, CHMe), 2.92 (3, singlet, CMe). Conclusive proof that the fractionation was in fact a resolution and not the separation of syn-anti isomers about the CN multiple bond[9] comes from the circular dichroism spectra shown in Figure 1. Three Cotton effects are found in the 500–300-mμ region of the spectrum whose positions clearly indicate that they arise from the chiral $(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)$ chromophore. It was noted above that secondary amines do not react with **1**; presumably this is because of severe steric requirements near the iron center making it most reasonable to assign the syn configuration to **8a** and **8b**. The metal center is stable to racemization. The resolved complexes are unchanged on refluxing in acetone.

This is the first example of the resolution of a chiral transition metal center in an organometallic compound which is stable to racemization and has the potential of retaining its optical activity during subsequent ligand transformations. In this connection, it should be pointed out that the first resolutions of transition metal compounds containing four different ligands by Brunner and coworkers[10] were not amenable to further reactions without racemization.

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[7] The reduction of **1** with $NaBH_4$ was previously reported.[4] However, these authors failed to notice the presence of the markedly less soluble **6** which is not eluted by chromatography in hexane; further, **4** and **6** have identical carbonyl stretches in the ir spectrum, ν (CO) 1912 cm^{-1} (hexane), such that the presence of **6** in the crude reaction mixture is not easily ascertained.

[8] R. F. Borch, *Tetrahedron Lett.*, 61 (1968).

[9] This type of isomer has been found in $Cr(CO)_5\{C(NHMe)Me\}$: E. O. Fischer, B. Heckl, K. H. Dötz, and J. Müller, *J. Organometal. Chem.*, **16**, P29 (1969).

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Received August 23, 1972

Chemiluminescence from the Reaction of the Hydrated Electron with Tris(bipyridyl)ruthenium(III)

Sir:

The hydrated electron, e_{aq}^-, is a rapid, powerful, and simple reducing agent[1] which on occasion has been postulated to give an excited-state product.[2,3] Undeniable evidence that such a product is formed would be that emission characteristic of a known product excited state is seen. We report here apparently the first observation of such emission along with an estimate of the chemiluminescent yield, ϕ_{cl}. The reaction is most simply represented by eq 1a,b, where bipy denotes bipyridyl.

$$\begin{tikzcd} & {[Ru(bipy)_3{}^{2+}]^*} \arrow[r] & Ru(bipy)_3{}^{2+} + h\nu \quad (1a) \\ Ru(bipy)_3{}^{3+} + e_{aq}^- \arrow[ur] \arrow[dr] & & \\ & \begin{bmatrix}\text{transition}\\ \text{state}\end{bmatrix}^{\ddagger} \arrow[r] & Ru(bipy)_3{}^{2+} \quad (1b) \end{tikzcd}$$

The strong room-temperature photoluminescence of $[Ru(bipy)_3{}^{2+}]^*$ at *ca.* 630 nm has been assigned as phosphorescence from a triplet charge transfer, ^3CT, state.[4–7] This same excited state can function as a sensitizer, either by excitation energy transfer[8] or as an excited-state reducing agent.[9] The state may also be produced chemically, by reduction of $Ru(bipy)_3{}^{3+}$ by hydroxide ion[10] and by hydrazine,[11] and derived from electrogenerated species in acetonitrile solutions of [Ru-

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[1] E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley, New York, N. Y., 1970.

[2] W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, **73**, 1941 (1969).

[3] M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, **94**, 1757 (1972).

[4] D. M. Klassen and G. A. Crosby, *J. Chem. Phys.*, **48**, 1853 (1968).

[5] J. N. Demas and G. A. Crosby, *J. Mol. Spectrosc.*, **26**, 72 (1968).

[6] F. E. Lytle and D. M. Hercules, *J. Amer. Chem. Soc.*, **91**, 253 (1969).

[7] J. N. Demas and G. A. Crosby, *ibid.*, **93**, 2841 (1971).

[8] J. N. Demas and A. W. Adamson, *ibid.*, **93**, 1800 (1971).

[9] H. Gafney and A. W. Adamson, unpublished work.

[10] D. M. Hercules and F. E. Lytle, *J. Amer. Chem. Soc.*, **88**, 4745 (1966).

[11] (a) F. E. Lytle and D. M. Hercules, *Photochem. and Photobiol.*, **13**, 123 (1971); (b) D. M. Hercules, *Accounts Chem. Res.*, **2**, 301 (1969).

$(bipy)_3]Cl_2$.[12] The present investigation was undertaken to see if chemiluminescence could be produced by means of a single-step reaction between well-defined reactants.

Sample handling techniques were essentially as described elsewhere.[13] Concentrated $Ru(bipy)_3{}^{3+}$ solutions were chemically generated by PbO_2 or Cl_2 oxidation of $Ru(bipy)_3Cl_2$[14] in aqueous 0.1 *N* H_2SO_4, filtered, saturated with He, and injected into the matrix yielding a final [Ru] of (0.2-1.0) × 10^{-3} *M*. The matrix consisted of triply distilled water, 0.2 *M* in *tert*-butyl alcohol for rapid $\cdot OH$ scavenging ($t_{1/2} \sim 11$ nsec), and 1 m*M* HOAc-2m*M* NaOAc for buffering. The pH of the irradiated solutions thus prepared was approximately 4.5, therefore limiting the reaction, $Ru(bipy)_3{}^{3+} + \cdot H$ (formed from $e_{aq}{}^- + H^+$, $t_{1/2} \sim 1$ μsec), to a minor role in reduction.[15] $e_{aq}{}^-$ was effectively the only radiation induced species involved and was observed to disappear from the irradiated solutions with $t_{1/2} \sim 10$-60 nsec (corresponding to $k_{[e_{aq}{}^- + Ru(bipy)_3{}^{3+}]} \simeq 6 \times 10^{10}$ M^{-1} sec^{-1}). The hydrated electrons were produced in the He or N_2O saturated solutions by 4-40 nsec single pulses of 15 MeV electrons from the Argonne National Laboratory's ARCO Linac.

Emission from the pulsed samples was monitored by an HTV R213 photomultiplier and Bausch and Lomb high-intensity monochromator combination. The spectrum, corrected for photomultiplier-monochromator response, is shown in Figure 1. The radiative lifetime, τ, for the $e_{aq}{}^- + Ru(bipy)_3{}^{3+}$ produced emitter was determined at all experimentally monitored wavelengths and consistently found to be 0.58 μsec at 25°. For comparison the emission spectrum of $Ru(bipy)_3{}^{2+}$ (excited at 453 nm) is also given.[16] τ, obtained by photoexcitation in aqueous 0.2 *M* *tert*-butyl alcohol with a pulsed N_2 laser, is 0.63 μsec.

That the emission arises from the reaction of the $e_{aq}{}^-$ with the complex is demonstrated by the greater than sixfold reduction of emission intensity upon N_2O saturation of the matrix $t_{1/2(N_2O + e_{aq}{}^-)} \sim 4.9$ nsec. Čerenkov stimulation of emission from $Ru(bipy)_3{}^{2+}$ (produced prior to the Linac pulse by thermal reduction) can be relegated to a minor role, since emission intensity from a pulsed 2 × 10^{-4} *M* $Ru(bipy)_3{}^{2+}$ solution was only 0.1 that observed on identically pulsing a 2 × 10^{-4} *M* $Ru(bipy)_3{}^{3+}$ sample. The yield of $Ru(bipy)_3{}^{2+}$, determined from its absorption at 453 nm, is $(1.0 \pm 0.1)/e_{aq}{}^-$; the dose absorbed by the solution was evaluated by "Super" Fricke dosimetry.[17]

ϕ_{cl} has been estimated as 0.015 ± 0.004 by comparing the detector response at 620 nm from a photoexcited $Ru(bipy)_3{}^{2+}$ solution of known photoluminescence yield, ϕ_{pl}, with the response obtained on reduction of $Ru(bipy)_3{}^{3+}$ by a known quantity of hydrated electrons[18] (the optical and detector systems being unchanged). This value of ϕ_{cl}, which is of the same order of magnitude as ϕ_{pl}, is relatively high for an *in vitro* chemiluminescent system.[20]

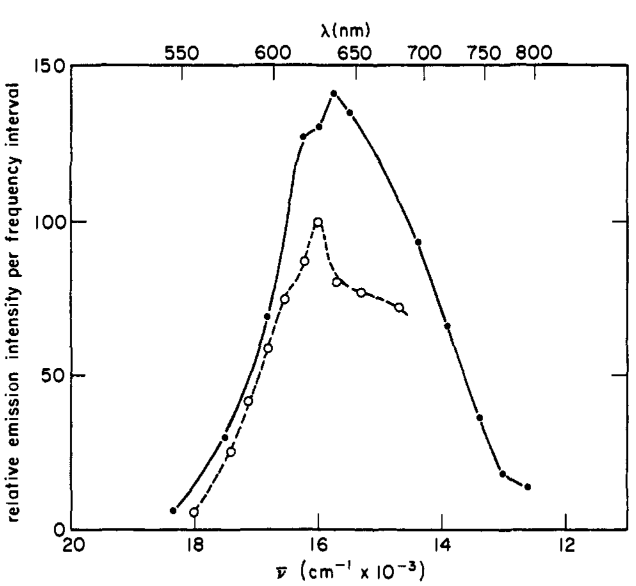

Figure 1. Chemiluminescence spectrum of $Ru(bipy)_3{}^{3+} + e_{aq}{}^-$ (○--○) and photoluminescence spectrum of $Ru(bipy)_3{}^{2+}$ (●—●).

We believe that these results do establish that reaction 1 indeed occurs and that the produced excited state is essentially the same ^3CT state observed in emission studies. We also find that the temperature variation of the emission yield (8-35°) corresponds to an activation energy of 1.5 kcal mol^{-1}; this compares with the value of 2.5 kcal mol^{-1} for the radiative decay following photoexcitation of $Ru(bipy)_3{}^{2+}$ in water.[6] Additional quantitative measurements of ϕ_{cl} and of the reaction kinetics are now in progress.

The production of the chemiluminescent state $[Ru(bipy)_3{}^{2+}]^*$ (with an excitation energy of *ca.* 2.0 eV) is consistent with the energetics of the reduction of $Ru(bipy)_3{}^{3+}$ by the powerful reducing agent $e_{aq}{}^-$, as well as by electrogenerated $Ru(bipy)_3{}^+$,[12] but not by weaker chemical one-electron reducing agents such as $TiCl_3$, which indeed failed to yield chemiluminescence,[11a] or $Cr(bipy)_3{}^{2+}$, which produced only very weak chemiluminescence.[21] In this context the strong chemiluminescence reported[11] to accompany the reduction of $Ru(bipy)_3{}^{3+}$ by the relatively weak reducing agents OH^- and N_2H_4 is somewhat surprising and is presumarly associated with steps involving high-energy intermediates (*e.g.*, $HO_2\cdot$ and N_2H_2) in the complex oxidations of these reductants to O_2 and N_2, respectively. Noteworthy in this respect is our preliminary observation that quite strong chemiluminescence ap-

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(12) N. E. Tokel and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 2862 (1972).

(13) J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, **68**, 1524 (1964).

(14) Prepared by the method of J. E. Ferguson and G. M. Harris *J. Chem. Soc. A*, 1293 (1966).

(15) In separate experiments conducted at lower pH, we have determined the rate constants for the reduction of $Ru(bipy)_3{}^{3+}$ by $H\cdot$ atoms and $(\dot{C}H_2)(CH_3)_2C(OH)$ radicals to be 1.7 × 10^9 and 1.3 × 10^8 M^{-1} sec^{-1}, respectively. While the reduction by $H\cdot$ also produces chemiluminescence (of as yet undetermined quantum yield), both of these reactions are too slow to account for the chemiluminescence described here and attributed to the hydrated electron.

(16) Photoluminescence was produced by W lamp output passed through a Bausch & Lomb monochromator and, at 90°, chopped and analyzed by a second monochromator and detected by an RCA C31025C photomultiplier, whose output was monitored by a Brower Lock-In voltmeter synchronized with the chopper.

(17) H. Fricke and E. J. Hart, *Radiat. Dosimetry*, **2**, 167 (1966).

(18) A 40-nsec pulse of Čerenkov light excited the aqueous $Ru(bipy)_3{}^{2+}$ at 25°. The intensity of absorbed light was measured by ferrioxalate actinometry.[19] The value of ϕ_{pl} used was 0.02 which was determined by comparison of corrected spectra for $Ru(bipy)_3{}^{2+}$ and quinine bisulfate in 1.0 *N* H_2SO_4 under steady illumination at 365 nm.

(19) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(20) K. D. Gundermann, *Angew. Chem., Int. Ed. Engl.*, **4**, 566 (1965).

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pears on mixing aqueous $NaBH_4$ with an acid solution of $Ru(bipy)_3^{3+}$; we also find luminescence on reduction of $Ru(bipy)_3^{3+}$ by aqueous H· atoms.

Acknowledgment. This work was performed under the auspices of the U. S. Atomic Energy Commission, with support through Grant GP-26600 to the University of Chicago from the National Science Foundation and through Contract DA-ARO-D-31-124-G87 between the U. S. Army Research Office (Durham) and the University of Southern California. We thank the Argonne Linac staff for experimental assistance.

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Received May 16, 1972

Evidence for Stepwise Solvation of Strontium Carbanion Salts in Ethereal Solvents

Sir:

The structure of ion pairs of alkali salts of carbanions and radical anions in aprotic solvents has been extensively studied in the last few years. The existence of contact or tight ion pairs and solvent-separated or loose ion pairs in these systems is now well documented.[1-3] Only recently has information on the structure of alkaline earth carbanions become available.[4,5]

In a previous communication we reported on the structure of fluorenylbarium and its crown ether complex in a few aprotic solvents such as tetrahydrofuran (THF) and dimethoxyethane (DME).[4] It was shown that this salt in THF over the temperature range 25 to −70° exists essentially as a tight ion pair. We now want to report evidence for a distinct stepwise solvation of the fluorenylstrontium ion pair in THF in the temperature range 20 to −100°. This process involves the formation of an asymmetrically solvated ion pair in which one of the fluorenyl moieties is separated from the strontium ion followed by the separation of the second fluorenyl unit to give a symmetrically solvated ion pair.

$$\mathrm{Fl^-M^{2+}Fl^-} \rightleftarrows \mathrm{Fl^-||M^{2+}Fl^-} \rightleftarrows \mathrm{Fl^-||M^{2+}||Fl^-}$$

The strontium salt was prepared in THF over a strontium mirror in the presence of a stoichiometric quantity of 1,1-diphenylethylene in an all-glass apparatus under high vacuum (10^{-6} mm) conditions. The visible spectrum of the recrystallized salt has maxima at 343, 435, and 458 nm and indicates a contact ion pair (Figure 1). On lowering the temperature the small shoulder at 372 nm, identifiable with separated ion pairs, increases rapidly in intensity. At −22° the two bands at 343 and 372 nm are approximately equal in intensity but at lower temperatures a large absorption band at 343 nm persists (Figure 1).[6] This behavior contrasts sharply with that of the alkali salts such as fluorenylsodium in this solvent where the transition from contact ion pairs to separated ion pairs is essentially complete at −70° and the contact ion pair absorption has disappeared.[1] The latter process is relatively straightforward

$$\mathrm{Na^+Fl^-} \overset{R}{\rightleftarrows} \mathrm{Na^+||Fl^-} \qquad \Delta H = -7.6\ \mathrm{kcal}$$

and the log R *vs.* $1/T$ plot is essentially straight over the entire temperature range (R = [separated ion pairs]/[contact ion pairs]). In the present case, however, the log R *vs.* $1/T$ plot is strongly curved (Figure 2).[7] Apparently the process is strongly exothermic ($\Delta H \simeq -12$ kcal), until approximately 50% of the contact ion pairs have been converted into separated ion pairs. The apparent enthalpy of the solvation process then decreases to a much lower value ($\Delta H \simeq -0.5$ kcal) and increases again at lower temperatures.

These observations suggest that the process is not represented by a simple one-step solvation process

$$\mathrm{Fl^-Sr^{2+}Fl^-} \overset{K_3}{\rightleftarrows} \mathrm{Fl^-||Sr^{2+}||Fl^-}$$

but possibly by a two-step process in which the fluorenyl ions become successively separated from the Sr^{2+} ion. The first step is expected to be highly exothermic, the second step much less so.

$$\mathrm{Fl^-Sr^{2+}Fl^-} \overset{K_1}{\rightleftarrows} \mathrm{Fl^-||Sr^{2+}Fl^-} \overset{K_2}{\rightleftarrows} \mathrm{Fl^-||Sr^{2+}||Fl^-}$$

From this scheme it can be seen that the ratio of [separated ion pairs] to [contact ion pairs] is given as shown in eq 1.

$$R = (1 + 2K_2)/(1 + 2/K_1) \qquad (1)$$

Taking the logarithm and differentiating with respect to $1/T$ gives the apparent enthalpy of the process, contact ion pairs ⇆ separated ion pairs (eq 2). From

$$\Delta H = (2/(2 + K_1))\Delta H_1 + (2K_2/(1 + 2K_2))\Delta H_2 \qquad (2)$$

(2) it follows that at high temperature, where K_1 and $K_2 \ll 1$, $\Delta H \simeq \Delta H_1$.

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(1) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **87**, 669 (1965); **88**, 307, 318 (1966).

(2) R. C. Roberts and M. Szwarc, *ibid.*, **87**, 5543 (1965); R. V. Slates and M. Szwarc, *ibid.*, **89**, 6043 (1967).

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(4) T. E. Hogen-Esch and J. Smid, *ibid.*, **91**, 4580 (1969).

(5) J. C. Favier, M. Fontanille, and P. Sigwalt, *Bull. Soc. Chim. Fr.*, **2**, 526 (1971); J. P. Pascault and J. Gole, *J. Chim. Phys.*, **68**, 442, 449 (1971); W. T. Ford, *J. Organometal. Chem.*, **32**, 27 (1971).

(6) Complete reversibility of the spectral phenomena and very low conductance of the solution assure that we are again dealing with ion-pair equilibria.

(7) The ratio R can as before (see ref 1) be evaluated using spectra of carbanion solutions existing as contact ion pairs or as separated ion pairs over the entire temperature range. In this case data on fluorenylbarium in THF and fluorenyllithium in DME were used to describe the behavior of contact and separated ion pairs. R was calculated on the assumption that the spectra of the two "types" of separated ion pairs, *e.g.*, of $\mathrm{||Fl^-}$ in $\mathrm{Fl^-Sr||Fl^-}$ and in $\mathrm{Fl^-||Sr||Fl^-}$, are identical. Extinction coefficients (ϵ) of contact and separated ion pairs are taken as 10,100 and 14,000, respectively, at 25°. The change of extinction coefficient with temperature expressed as $-\mathrm{d}(\epsilon_{T°}/\epsilon_{20°})/\mathrm{d}T$ was determined as 4.0×10^{-3} and 6.0×10^{-3} for contact and separated ion pairs, respectively. The contribution of separated ion pairs at 343 nm defined as $OD_{343}/OD_{max\ 372}$ and the contribution of the contact ion pairs at 373 nm ($OD_{372}/OD_{max\ 343}$) were determined as a function of temperature. At −76°, for instance, these values were 0.26 and 0.27, respectively. Using these data one calculates that the increase of OD of the contact ion pair at 343 nm on lowering the temperature is only apparent. For instance, the corrected absorption of the contact ion pair at −76° is only about 0.60.