Table II. Many-Body Interaction Energies[a]

$Be^{2+}–3H_2O$, $R(Be^{2+}–O) = 1.50$ A
$E^{(1)}(Be^{2+}) = -13.610806$ au
$E^{(1)}(H_2O) = -76.009255$ au
$E^{(2)}(Be^{2+}–OH_2)^b = -150.6$ kcal/mol
$E^{(2)}(2H_2O$, parallel$)^c = 6.8$ kcal/mol
$E^{(2)}(2H_2O$, perpendicular$)^d = 24.3$ kcal/mol
$E^{(3)}(3H_2O) = -3.5$ kcal/mol
$E^{(3)}(Be^{2+}–2H_2O$, parallel$) = 1.50$ kcal/mol
$E^{(3)}(Be^{2+}–2H_2O$, perpendicular$) = 36.4$ kcal/mol
$E^{(4)}(Be^{2+}–3H_2O) = -4.0$ kcal/mol

$Li^+ \cdots (OH_2)_a \cdots (OH_2)_b$, $R(O_1–O_2) = 2.7$ Å, $R(Li^+–O_1) = 1.85$ Å
$E^{(1)}(Li^+) = -7.235987$ au
$E^{(1)}(H_2O) = -76.046536$ au
$E^{(2)}(Li^+ \cdots (O_2H_2)_a) = -37.2$ kcal/mol
$E^{(2)}(Li^+ \cdots (O_2H_2))_b = -6.6$ kcal/mol
$E^{(2)}(H_2O) \cdots (H_2O)_b) = -4.1$ kcal/mol
$E^{(3)}(Li^+ \cdots (OH_2)_a \cdots (OH_2)_b = -4.5$ kcal/mol

[a] Terms calculated using eq 1; for example, $E^{(3)}(3H_2O)$ was determined by carrying out SCF calculations on (a) the three waters, (b) two waters parallel $= E^{(2)}(2H_2O$, parallel), (c) two waters perpendicular $= E^{(2)}(2H_2O$, perpendicular), and (d) the energy of an isolated water. Then $E^{(3)} = E$(SCF for 3 waters) $- E^{(2)}(2H_2O$, parallel) $- 2E^{(2)}(2H_2O$, perpendicular) $- 3E^{(1)}(H_2O)$. [b] A negative $E^{(2)}$ means the two bodies are at a lower energy than the sum of $E^{(1)}$. [c] Parallel means one water along the x axis and the other along the $-x$ axis. [d] Perpendicular means one water along the x axis and the other along the y.

$Li^+–H_2O$ complex formation and placing the second water in a position to form a hydrogen bond with the first water. The results of SCF calculations[8] on the three molecules and the three two-body combinations, at the minimum O–O distance between water molecules, are presented in Table II. There are two points of special interest: (1) the minimum energy O–O distance has been shortened from the 3.0 Å found in the water dimer to 2.7 Å; (2) the three-body interaction energy $E^{(3)}$ for this configuration is −4.5 kcal/mol, indicating that the hydrogen bond is 8.6 kcal/mol,[9] in comparison to the 5.0 kcal/mol found for the optimum H bond in the water dimer.[10] These results are of considerable interest, because they demonstrate the magnitude of the effect that monoatomic cations can have on the energetics and geometries of H bonding between water molecules and the electrostriction that these cations might bring about.

The extension of these studies to other cations and ions, an analysis of ir properties of cation hydrates, and a decomposition of the energy of complex formation into electrostatic, charge-transfer, and polarization terms will be reported separately.

Acknowledgment. We gratefully acknowledge support of this work by the Academic Senate of the University of California, San Francisco, National Science Foundation (GP31564), and the National Institutes of Health (GM 19269). We thank Fritz Schaefer and Dean Liskow for computational assistance.

Peter A. Kollman,* Irwin D. Kuntz
Department of Pharmaceutical Chemistry, School of Pharmacy
University of California, San Francisco, California 94122

Received September 23, 1972

---

(8) The same basis set as in the monohydrate calculations was used here.

(9) We estimate our H-bond strength by combining $E^{(2)}[(H_2O)_a \cdots (H_2O)_b]$ with $E^{(3)}(Li^+ \cdots OH_a \cdots OH_b)$, since the main effect of the lithium is to increase the positive charge on the water hydrogens $[(H_2O)_a]$ and to increase its ability to function as a proton donor. These calculations are similar to those carried out by Diercksen and Kraemers,[3a] who interpreted their calculations in terms of an H-bond strength of 16.1 kcal/mol. These authors have, we feel, incorrectly included the attraction of the lithium for the more distant water $[E^{(2)}(Li^+ \cdots (OH)_2)_b]$ as part of the H-bond strength. Thus, the increase in H-bond strength due to the presence of Li^+ is significant but not nearly as "drastic" as suggested.[3a]

(10) The optimum H bond for the water dimer with this basis set had an O–O separation of 3.0 Å with an H-bond strength of 5.0 kcal/mol. The other geometrical parameters were kept at the optimum values found in ref 5.

Reactions of $[(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{C(OEt)CH_3\}]BF_4$ with Nucleophiles. Evidence for Carboxonium Rather than Carbenoid Behavior

Sir:

Electrophilic alkylations of $M'\{C(OLi)R\}$, where $M' = M(CO)_5$[1] or $M(CO)_4PPh_3$[2] (M = Cr, Mo, or W), $(h^5\text{-}C_5H_5)M(CO)_2$ (M = Mn[1] or Re[3]), or $M''COR$, where $M'' = (h^5\text{-}C_5H_5)M(CO)_xPPh_3$[4] (M = Fe or Ru, $x = 1$ and M = Mo, $x = 2$), are generally regarded as giving rise to "metal–carbene" complexes. However, it seems appropriate, in view of their reactivity patterns, to consider them as metal-stabilized carboxonium rather than carbenoid compounds.

Our results on the reaction of $[(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{C(OEt)CH_3\}]BF_4$[4] (**1**) with a variety of nucleophiles show the characteristic modes[5] of behavior of purely organic carboxonium salts which has led to the description of the latter as ambident cations.[5,6]

The salt **1** undergoes dealkylation when treated with NaI in THF. Ethyl iodide is eliminated by rupture of the carbon to oxygen single bond to give $(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_3)$ (**2**) and is in essence the reverse of the alkylation which produces **1**.

Proton abstraction from the carbon atom β to the oxonium center occurs when **1** is treated with ethoxide ion in ethanol. The resulting vinyl ether $(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{C(OEt)CH_2\}$ (**3**), the conjugate base of **1**, can be protonated by HBF_4–propionic anhydride mixtures to re-form **1**. Reduction of **3** with either H_2/PtO or B_2H_6 in EtOH gives the σ-α-ethoxyethyl derivative $(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{CH(OEt)CH_3\}$ (**4**). This reaction introduces a second chiral center at the carbon α to the chiral metal center. The pairs of enantiomers (*RR,SS* and *RS,SR*) have clearly different nmr spectra in the methyl region and are readily separable by fractionation from hexane. Nmr spectra methyl region (δ in acetone-d_6): less soluble enantiomeric pair (mp 130.5–131°) 1.08 (3, triplet, $J = 6.8$ Hz, CH_2Me), 1.55 (3, doublet, $J = 6.2$ Hz, CHMe); more soluble enantiomeric pair (mp 114–115°) 0.94 (3, triplet, $J = 6.8$ Hz, CH_2Me), 1.52 (3, doublet, $J = 6.2$ Hz, CHMe). Careful monitoring of the reaction shows that both pairs are produced in approximately equal amounts which indicates no significant asymmetric induction occurred on reduction. Treatment of **3** with methoxide ion in methanol gives rise to the methoxy vinyl derivative $(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{C(OMe)CH_2\}$ (**5**).

The treatment of **1** with an equimolar amount of

---

(1) E. O. Fischer and A. Maasböl, *Chem. Ber.*, **100**, 2445 (1967).

(2) E. O. Fischer and R. Aumann, *ibid.*, **102**, 1495 (1969).

(3) E. O. Fischer and A. Reidel, *ibid.*, **101**, 156 (1968).

(4) M. L. H. Green, L. C. Mitchard, and M. G. Swanwick, *J. Chem. Soc. A*, 794 (1971).

(5) H. Perst, "Oxonium Ions in Organic Chemistry," Academic Press, New York, N. Y., 1971.

(6) S. Hünig, *Angew. Chem., Int. Ed. Engl.*, **3**, 548 (1964).

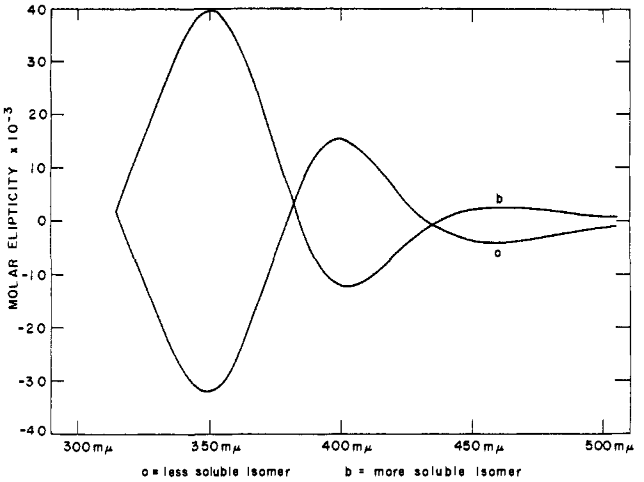

Figure 1. Circular dichroism spectra of the diastereomers of $[(h^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{C((S)\text{-}NHCHMePh)Me\}][BF_4]$.

$NaBH_4$ 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.

---

[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).

[10] H. Brunner, *Angew. Chem., Int. Ed. Engl.*, 10, 249 (1971).

A. Davison,* D. L. Reger
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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.

$$\mathrm{Ru(bipy)_3^{3+}} + e_{aq}^- \begin{array}{l} \nearrow [\mathrm{Ru(bipy)_3^{2+}}]^* \longrightarrow \mathrm{Ru(bipy)_3^{2+}} + h\nu \qquad \text{(1a)} \\ \searrow \begin{bmatrix}\text{transition}\\ \text{state}\end{bmatrix}^{\ddagger} \longrightarrow \mathrm{Ru(bipy)_3^{2+}} \qquad \text{(1b)} \end{array}$$

The strong room-temperature photoluminescence of $[\mathrm{Ru(bipy)_3^{2+}}]^*$ at *ca.* 630 nm has been assigned as phosphorescence from a triplet charge transfer, ^{3}CT, 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 $\mathrm{Ru(bipy)_3^{3+}}$ by hydroxide ion[10] and by hydrazine,[11] and derived from electrogenerated species in acetonitrile solutions of [Ru-

---

[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).