in accord with this assignment.[34] Finally, it should be mentioned that theoretically it should be possible for the bridging-ligand π^* energy level to be higher than that in bipyridine, in which case the $d\pi \rightarrow \pi^*$ assignments for mononuclear complexes would be reversed.

Registry No. Ru(bpy)$_2$BL(1)(PF$_6$)$_2$, 82849-33-0; [Ru-(bpy)$_2$]$_2$BL(1)(PF$_6$)$_4$, 82849-35-2; Ru(bpy)$_2$BL(2)(PF$_6$)$_2$, 82849-37-4; [Ru(bpy)$_2$]$_2$BL(2)(PF$_6$)$_4$, 82864-91-3; Ru(bpy)$_2$(bpyrm)(ClO$_4$)$_2$, 82864-92-4; [Ru(bpy)$_2$]$_2$bpyrm(ClO$_4$)$_4$, 82849-38-5; Ru(bpy)$_2$BL-(1)(ClO$_4$)$_2$, 82849-40-9; [Ru(bpy)$_2$]$_2$BL(1)(ClO$_4$)$_4$, 82849-41-0; BL(2), 82849-31-8; Ru(bpy)$_2$Cl$_2$, 15746-57-3; 1,2,4,5-benzene-tetramine tetrahydrochloride, 4506-66-5; 2,2′-bipyridyl, 366-18-7.

Supplementary Material Available: A listing of elemental analyses for reported compounds (1 page). Ordering information is given on any current masthead page.

(34) Braunstein, C.; Baker, A. D.; Gafney, H. D.; Strekas, T. C. "Abstracts of Papers", 182nd National Meeting of the American Chemical Society, New York, Aug 23–28, 1981; American Chemical Society: Washington, DC, 1981; INOR 250.

Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer. 57. A Reverse Kinetic Salt Effect in Some Inner-Sphere Reductions by Chromium(II)[1]

Vangalur S. Srinivasan[2] and Edwin S. Gould*

The reactions of mono(carboxylato) derivatives of cobalt-(III) with the usual metal-center reductants (bimolecular reactions between cations) should exhibit positive kinetic salt effects; i.e., they should be accelerated by addition of a nonparticipating electrolyte.[3] Past reports of such accelerations[4] have considered them mainly as sidelights subsidiary to more interesting mechanistic facets. This communication describes three such systems in which the salt effect is substantial and takes a direction opposite to that expected.

Experimental Section

Materials. Lithium perchlorate[5] and solutions of Cr(ClO$_4$)$_2$,[4a] V(ClO$_4$)$_2$,[6] and Eu(ClO$_4$)$_2$[7] were prepared as described. Sodium

(1) Sponsorship of this work by the National Science Foundation is gratefully acknowledged.
(2) On leave from Vivekanada College, Mylapore, Madras, India.
(3) See, for example: (a) Weston, R. E., Jr.; Schwarz, H. A. "Chemical Kinetics"; Prentice-Hall: Englewood Cliffs, NJ, 1972; p 165. (b) Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; p 172.
(4) See, for example: (a) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1320. (b) Liang, A.; Gould, E. S. *Ibid.* **1970**, *92*, 6791. (c) Gould, E. S. *Ibid.* **1970**, *92*, 6797.
(5) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.
(6) (a) Guenther, P. R.; Linck, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 3769. (b) Linck, R. G. *Inorg. Chem.* **1970**, *9*, 2529.
(7) (a) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6673. (b) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639.

Table I. Variation, with Ionic Strength, of Specific Rates for Reduction of Some (Carboxylato)cobalt(III) Complexes

reductant	[H⁺], M	μ, M	k,[a] M^{-1} s^{-1} 2-isomer	4-isomer
A. 2- and 4-Formyl-Substituted μ-Benzoato Co^{III} Dimers (I and II)				
Cr^{2+}	0.10	0.10	11.5	42
	0.10	0.25	27[c]	67,[b] 73[c]
	0.10	0.50	25,[b] 29[c]	
	0.10	0.75	31[c]	80,[b] 82[c]
	0.20	1.00		95[b]
	0.50	1.00		97[b]
	1.00	1.00	37	95
	0.10	1.50		73,[b] 71[c]
	0.10	2.00	29,[b] 26[c]	67,[b] 51[c]
	2.00	2.00	28	67
	0.10	4.00	15.0,[b] 14.6[c]	27,[b] 23[c]
	1.00	4.00	13.7,[b] 16.2[c]	23,[b] 27[c]
	4.00	4.00	12.8	29
V^{2+}	0.10	1.00	0.23[b]	0.126[b]
	1.00	1.00	0.25	0.130
	1.00	4.00		0.096[b]
	2.00	4.00	0.22[b]	
	4.00	4.00	0.25	
Eu^{2+}	0.10	1.00	0.049[b]	0.67[b]
	1.00	1.00	0.058	0.70
	2.00	4.00	0.036[b]	
	4.00	4.00	0.038	
B. 2- and 4-Formylbenzoato Complexes of (NH$_3$)$_5$Co^{III} (III)				
Cr^{2+}	0.10	0.10		43
	0.10	0.25		57,[b] 48[c]
	0.10	1.00		62,[b] 66[c]
	1.00	1.00	73	
	0.10	2.50		60,[b] 60[c]
	0.10	3.50		43,[b] 44[c]
	0.10	4.00	77,[b] 73[c]	34,[b] 30[c]
	1.00	4.00	69,[b] 69[c]	
C. μ-Pyruvato Co(III) Dimer (IV)				
Cr^{2+}	0.10	0.10	10	
	0.10	1.00	37,[b] 20[c]	
	0.10	4.00	40,[b] 38[c]	
D. HCOOCo(NH$_3$)$_5$$^{2+}$				
Cr^{2+}	1.00	1.00	6.8	
	0.10	4.00	7.9,[b] 7.6[c]	
	1.00	4.00	7.3,[b] 7.0[c]	

[a] Specific rates at 25 °C. Values for the dimeric complexes refer to the rate of disappearance of the dimer. [b] Supporting electrolyte HClO$_4$ + LiClO$_4$. [c] Supporting electrolyte HClO$_4$ + NaClO$_4$.

perchlorate solution was prepared by treating reagent grade NaHCO$_3$ with 70% HClO$_4$, adjusting the pH to 4, diluting to the desired volume, and then purging with N$_2$ to remove dissolved CO$_2$. Cobalt complexes were available from a previous study.[8]

Rate Measurements. Rates were estimated from measurements of absorbance changes on a Cary Model 14 or Beckman Model 5260 recording spectrophotometer as described.[4a,7] Earlier studies[4a,8] demonstrated that reactions were first-order each in reductant and Co(III), but experiments in this series were carried out under pseudo-first-order conditions with at least a 10-fold excess of reductant and were monitored at 524 or 502 nm (the low-energy maximum of the Co^{III} complexes). Reactions were followed for at least 4 half-lives. Rate constants evaluated from successive half-life values in a single run agreed to within 5%. Specific rates obtained from replicate runs checked to better than 7%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Results and Discussion

Kinetic data appear in Table I. The few entries for the Cr(II) reductions of the μ-pyruvato dimer (IV) and for the formato monomer indicate that these reactions exhibit salt

(8) Srinivasan, V. S.; Singh, A. N.; Weighardt, K.; Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1982**, *21*, 2531.

I

II

III (R = 2- or 4-CHO)

IV
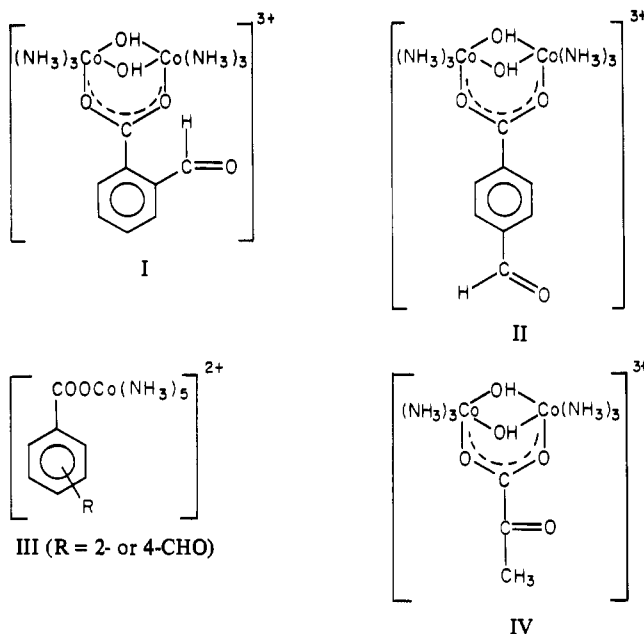
effects in the expected direction. Moreover, there is no sign of partial protonation of the lead-in site (which would retard reduction[9]) at acidities below 1.0 M.

With the 2- and 4-formyl-substituted μ-benzoato dimers (I and II), Cr(II) rates are seen to increase with ionic strength in the range 0.10–1.0 M, reach maxima near 1.0 M, and then decrease by almost 70% between 1.0 and 4.0 M. These rate maxima are observed with $HClO_4$, $NaClO_4$, $LiClO_4$, and various combinations of these as supporting electrolytes. A similar, but somewhat less intense, trend occurs with the Cr^{2+} reduction of the monomeric 4-formylbenzoato complex (III, R = 4-CHO),[10,11] whereas the data for the V^{2+} reduction of the 4-formyl dimer and for the Eu^{2+} reduction of its 2-formyl isomer hint at only a marginal effect of the same kind.

Evidence has been presented[8] that observed rates of reduction of μ-carboxylato cobalt(III) dimers of the type being considered are determined by reduction of the first of the two Co(III) centers and that the predominant mechanism for reduction of the μ-formylbenzoato and μ-pyruvato (IV) dimers,[8,12] as well as that of the 4-formylbenzoato monomer,[13] entails attack by the reducing center at the unbound carbonyl function.

The limitations of the Brønsted–Bjerrum–Christiansen relationship between the specific rate of an ionic reaction and the ionic strength of the medium are well recognized[14] and are known to become particularly severe at very high values of μ. We nevertheless have encountered no previous instance in which the kinetic salt effect in aqueous medium suffers a reversal in direction. The possibility that what we are seeing stems from a shift in the hydration equilibrium –CHO $\rightleftharpoons$ –CH(OH)$_2$ associated with the aldehyde group, i.e., that a greater fraction of the oxidant is converted to its much less

reactive[15] diol form at higher ionic strengths, appears to be ruled out by the absence of significant decreases in the carbonyl absorbance of the oxidant in solution as the ionic strength is increased.[16]

For each of these inner-sphere reactions, the observed rate constant is determined jointly by the association constant of the Co(III)–Cr(II) precursor complex and the specific rate of internal electron transfer within this precursor. The normal positive salt effect is almost certainly due, in major part, to the increased conversion of the reactants to the precursor at the greater ionic strength, i.e., to a shift in this preequilibrium involving the aggregation of charge. We attribute the reversals observed in the few cases noted here to deceleration of internal transfer reflecting the drop in activity of water at high ionic strengths. It has been pointed out[17] that a precursor complex featuring Cr(II) bound to a carbonyl group allows no effective overlap between the acceptor π orbitals of the organic bridging group and the d_{z^2} orbital which accommodates the reducing electron of Cr(II) unless the ligand environment about Cr(II) is unsymmetrically distorted, a distortion in which water molecules in the second coordination sphere of this center are presumed to play a major part. Of the ten water molecules in this secondary sphere, the four that are hydrogen bonded to the two primary water ligands aligned with the d_{z^2} lobe may be considered to be part of the activated complex for internal transfer.

The activity of water in an aqueous solution is proportional to its partial vapor pressure. Although vapor pressure measurements have been made for concentrated solutions of $HClO_4$,[18] $LiClO_4$,[19] and $NaClO_4$[19] (each at 25 °C), we find no reports of such studies of systems featuring two or more perchlorates at high concentrations. However, values for $HClO_4$ solutions lie so close to those for $LiClO_4$ solutions having the same molar concentrations that we may assume that partial replacement of $HClO_4$ by $LiClO_4$ in concentrated aqueous solutions results in only slight changes in the activity of water (an expedient that is less admissible for $NaClO_4$–$HClO_4$ systems). In particular, interpolation of Robinson's data[18] allows us to estimate the ratio of the activity of water in 1.0 M $HClO_4$ to that in 4.0 M $HClO_4$ as 0.960/0.710 (or 1.35), whereas Jones' data[19] lead to the ratio 0.962/0.740 (or 1.30) for 1.0 and 4.0 M $LiClO_4$. Hence, for $HClO_4$–$LiClO_4$ systems, the activity of water is about 1.3 times as great at $\mu = 1.0$ as at $\mu = 4.0$. If it is assumed that the action of four molecules of water in the secondary coordination sphere is necessary for the act of internal electron transfer, this activity ratio should be reflected in an acceleration factor of 1.3^4 or 2.8 in going from $\mu = 4.0$ to $\mu = 1.0$. Agreement with the observed ratios (which lie between 2.3 and 3.2) may be considered reasonable since the implied model is very much an oversimplification. At ionic strengths below about 1.0, where the activity of water is very nearly constant, the more usual positive salt effect predominates.

Note that the arguments presented do not apply to reductions by V^{2+} or Eu^{2+}, for with each of these reductants, the migrating electron occupies a metal orbital (d_{yz} or f_{z^3}) having

(9) See, for example: (a) Barrett, M. B.; Swinehart, J. H.; Taube, H. *Inorg. Chem.* **1971**, *10*, 1983. (b) Thomas, J. C.; Reed, J. W.; Gould, E. S. *Ibid.* **1975**, *14*, 1696.

(10) Since the rate of the Cr(II) reduction of the 4-CHO monomer (III) has been shown to be strongly acid dependent,[11] data for this oxidant were taken at a single concentration of $HClO_4$.

(11) Gould, E. S. *J. Am. Chem. Soc.* **1965**, *87*, 4730.

(12) Hyde, M. R.; Wieghardt, K.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1976**, 690.

(13) Zanella, A.; Taube, H. *J. Am. Chem. Soc.* **1972**, *94*, 6403.

(14) See, for example: (a) Perlmutter-Hayman, B. *Prog. React. Kinet.* **1971**, *6*, 240. (b) Pethybridge, A. D.; Prue, J. E. *Prog. Inorg. Chem.* **1972**, *17*, 327.

(15) Gould, E. S.; Johnson, N. A.; Morland, R. B. *Inorg. Chem.* **1976**, *15*, 1929.

(16) The carbonyl absorbance maximum for the 2-formyl dimer (I) was found to lie at 292 nm ($\epsilon = 5.7 \times 10^3$ M^{-1} cm^{-1}) in 0.1 M $HClO_4$ and 294 nm (5.7×10^3) in 4.0 M $LiClO_4$. The maximum for the 4-formyl dimer (II) was at 255 nm ($\epsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}) in 0.1 M $HClO_4$ and at 257 nm (3.1×10^4) in 4.0 M $LiClO_4$. Shoulders were at 255 nm for the 2-isomer and 300 nm for the 4-isomer. We thank Dr. N. Rajasekar for aid in these measurements.

(17) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

(18) (a) Robinson, R. A.; Baker, O. J. *Trans. R. Soc. N. Z.* **1946**, *76*, 250; *Chem. Abstr.* **1947**, *41*, 5000d. (b) Robinson, R. A.; Stokes, R. H. *Trans. Faraday Soc.* **1949**, *45*, 612.

(19) Jones, J. H. *J. Phys. Chem.* **1947**, *51*, 516.

the same symmetry character as the π orbitals of the carbonyl bridge;[17] hence, no distortion of the coordination sphere of the reductant is required for overlap. Finally, it appears that the importance of overlap between reductant and bridge orbitals increases sharply as the π system of the bridge is extended by interposition of an aromatic ring in conjugation with the carbonyl function. Thus, the reverse salt effect is not observed in the Cr^{2+} reduction of the μ-pyruvato dimer (IV), in which the bridging group is a lone keto carbonyl, nor in the formato monomer, in which the bridge is a carboxyl carbonyl.[20]

(20) Chromium(II) reduction of the 2-formylbenzoato monomer (III, R = 2-CHO) exhibits only the expected positive salt effect. Attack at the aldehydo group has been shown to play only a minor role in this reduction.[8]

Communications

Improved Synthesis of $UCl_3(THF)_x$ and the Preparation of 15-Crown-5 Derivatives of Trivalent Uranium

Sir:

Since our first report of the synthesis of $UCl_3(THF)_x$ (THF = tetrahydrofuran),[1] its utility as a starting material for trivalent uranium syntheses has been demonstrated in our laboratories[2] and in others.[3] The sodium hydride reduction of uranium tetrachloride has proved convenient in our hands as a reproducible route to this starting material; however, the variable activity of commercial sodium hydride as well as problems associated with further reduction of the uranium to lower valent species has necessitated exacting control over reaction times as well as solvent amounts. While eliminating some of these problems, an alternative procedure reported by Andersen[3] still requires exacting stoichiometric control of reagents since excess sodium naphthalide will easily reduce $UCl_3(THF)_x$. Also in those instances where naphthalene interferes in subsequent reactions, an additional purification step is required.

In this report we present an improved synthesis of UCl_3-$(THF)_x$, which utilizes excess sodium carbide as the reducing agent and provides marked improvements over the two previously described routes to this key material. A convenient diagnostic for the purity of this reagent is also discussed as part of the chemistry of $UCl_3(THF)_x$ with 15-crown-5 and benzo-15-crown-5.

Experimental Section. All manipulations were performed under a dry nitrogen atmosphere by using standard Schlenk techniques or by using standard vacuum techniques. All solvents used in this study were reagent grade and were dried prior to use. UCl_4 was prepared by literature procedures.[4] Sodium carbide was purchased from Alfa Chemicals and used as received. Benzo-15-crown-5 and 15-crown-5 were obtained from Parish Chemical Co. and were used without further purification. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

$UCl_3(THF)_x$. Uranium tetrachloride (0.38 g, 1 mmol) and Na_2C_2 (0.35 g, 5 mmol) were loaded into a 100-mL reaction vessel in the drybox, and 80 mL of dry, degassed THF was condensed onto the solid. When the mixture was warmed to room temperature, an immediate color change from green to purple was observed. Excess Na_2C_2, NaCl, and carbon were filtered from the stirred solution after 2 h, and the THF solution of $UCl_3(THF)_x$ was characterized as previously reported.[1] Such solutions were found to contain ca. 0.8 mmol

(1) Moody, D. C.; Odom, J. D. *J. Inorg. Nucl. Chem.* **1979,** *41,* 533.
(2) Moody, D. C.; Penneman, R. A.; Salazar, K. V. *Inorg. Chem.* **1979,** *18,* 208.
(3) Andersen, R. A. *Inorg. Chem.* **1979,** *18,* 1507.
(4) Hermann, J. A.; Suttle, J. F. *Inorg. Synth.* **1957,** *5,* 143.

of $UCl_3(THF)_x$. No evidence of further reduction was observed upon stirring the reaction solutions overnight prior to filtration.

$UCl_3(THF)_x$ + **15-Crown-5.** The above solutions of 0.8 mmol of $UCl_3(THF)_x$ were filtered onto excess (0.5 mL) 15-crown-5 in 15 mL of THF. Quantitative precipitation of red UCl_3(15-crown-5) occurred as the reaction was stirred overnight, and when the mixture was filtered through a fine frit and the solid was vacuum dried, 0.41 g (0.73 mmol) of product was isolated from the frit. Anal. Calcd for $UCl_3O_5C_{10}H_{20}$: C, 21.27; H, 3.57; U, 42.15; Cl, 18.84; O, 14.17. Found: C, 21.86; H, 3.85; U, 38.97; Cl, 20.20; O, 15.25. The filtrate from the above reaction was colorless to pale green depending on residual U^{IV}·15-crown-5 present.

A thermogravimetric analysis on UCl_3(15-crown-5) (5.9 mg) indicated decomposition at 308 °C and leveled off at 488 °C with a 50% weight loss. Continued heating under moist oxygen produced 2.89 mg of U_3O_8, corresponding to 41.5% U.

$UCl_3(THF)_x$ + **Benzo-15-crown-5.** Reaction of 0.8 mmol of $UCl_3(THF)_x$ in 80 mL of THF with 1 g of benzo-15-crown-5 in 20 mL of THF slowly precipitated UCl_3(benzo-15-crown-5) as a fine red powder. After the mixture was stirred overnight, the precipitate was filtered and vacuum dried, yielding 0.39 g (0.64 mmol) of product and a red filtrate. A quantitative precipitation was observed when 1.5 g or more of benzo-15-crown-5 was used. Anal. Calcd for $UCl_3O_5C_{14}H_{20}$: C, 27.44; H, 3.29; U, 38.85; Cl, 17.36; O, 13.06. Found: C, 27.21; H, 3.44; U, 39.02; Cl, 17.19; O, 12.85.

Results and Discussion. Reduction of uranium tetrachloride by excess sodium carbide in THF has proved to be a most convenient route to the key starting reagent, $UCl_3(THF)_x$. Several advantages over previous syntheses are readily discernible, the most important being that no further reduction past U(III) occurs with this reducing agent. In addition, precise control of stoichiometry is not necessary and all by-products (NaCl and C_n, in addition to the excess Na_2C_2) are insoluble and thus easily removed by filtration.

While previous work in our laboratories[2] had established 18-crown-6 as a good ligand for trivalent uranium, an examination of the cavity diameter of 15-crown-5 suggested an even better match for U(III). Thus the first uranium(III) complexes with 15-crown-5 and benzo-15-crown-5 were prepared. A comparison of the thermal gravimetric analysis on UCl_3-(15-crown-5) with that reported for UCl_3(18-crown-6)[2] supports this contention of increased stability for the 15-crown-5 derivatives in that decomposition occurs at 200 °C for the latter and at 308 °C for the former.

An interesting aside has also resulted from this 15-crown-5 chemistry pertaining to a convenient method of testing the