result in part from increased interaction of the unpaired electron with the deuterium on the D_2O adduct.

A temperature-dependent line width was observed by Garif'yanov, *et al.*[18a] For a 0.3 M solution of $TiCl_3 \cdot 6H_2O$ in methanol, the line width increased from 7 G at $-33°$ to 11 G at $+87°$ which they attributed to vibrational interaction between the ligands and the metal. At temperatures above $+15°$, we observe an increase in the line width of both species. This suggests the additional possibility of interconversion between two species as a mechanism of line broadening. At lower temperatures the line shape and the apparent g factor of the spectrum of the $TiCl_3$–H_2O–CH_3OH system would depend on the relative amounts of A and B species present, which is a function of the concentration of $TiCl_3$ and H_2O.

The two dominant complexes of titanium(III) chloride in methanol appear to be the chloro and dichloro complexes. The entire equilibrium, however, may include other complexes as well as cis and trans isomers, and thus we are not ready to evaluate the behavior of the entire system.

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Reinvestigation of Malonate as an Electron-Transfer Bridge. A Medium Effect

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Recent observations made in our laboratory have caused us to examine acid-catalyzed electron-transfer reactions between two positively charged metal complexes. Ignoring the possibility of a three-bodied collision, rate terms of the form $k_h(M_a^{n+})(M_b^{m+})(H^+)$ reflect transition states wherein a cation donates or accepts an electron from another cation which is tightly associated with a proton. Unless some special mitigative factor comes into play, the formation of this transition state will be electrostatically unfavorable relative to formation of the lower charged transition state described by the rate term $k(M_a^{n+})(M_b^{m+})$; *e.g.*, Barrett, Swinehart, and Taube[1] have shown that the rate of chromium(II) reduction of protonated acetatopentaamminecobalt(III) is slower than the rate of reduction of the unprotonated ion. Two such factors which increase the relative efficiency of the k_h pathway have been well documented. (1) Taube and Gould[2] have reviewed the considerable evidence for a k_h term in the chromium(II) reduction of pentaamminecobalt(III) complexes of dicarboxylic acids in which the two carboxylate groups are connected by a conjugated bond system. They suggested that the k_h term reflects chromium(II) attack at the remote carboxylate while the proton resides on the Co(III)-bound carboxylate. This protonation improves conjugation between the two metal centers and thus electron transfer is promoted. (2) Haim and coworkers[3] have studied the inner-sphere reduction of *trans*-A_4CoXY^{n+} complexes, where A is either ammonia or half an ethylenediamine, Y is the bridging ligand, and X is the ligand situated trans to Y. They observed a k_h path whenever X is basic enough (*e.g.*, acetate or azide) to provide a protonation site and ascribed the effect to a lowering of the energy of the acceptor orbital in the protonated form relative to that in the unprotonated species.

There exists in the literature an example of an acid-catalyzed cation–cation electron-transfer reaction that apparently does not fit into either of the above two categories. The reduction of malonatopentaamminecobalt(III) by chromium(II) was originally reported by Svatos and Taube[4] and later confirmed by Butler and Taube[5] to be controlled by a rate law in which there is a k_h term. It was also reported that this term was not present in the reduction of dialkylmalonato complexes. An interpretation of these observations, based on the relative acidity of the methylene protons of malonic acid, has been offered,[4–6] the significance of which has been to extend the general consideration of various factors which may promote the relative efficiency of k_h pathways. This anomalous example of acid-catalyzed electron transfer through a nonconjugated acid is based upon limited data which were obtained with sodium perchlorate as a supporting electrolyte.[7] It is now well established that the use of sodium perchlorate, rather than lithium perchlorate, is likely to have a significant effect on the measured acid dependencies of redox reactions.[5,8] Therefore we thought it worthwhile to reinvestigate the acid dependence of the malonato and dialkylmalonato reactions, using lithium perchlorate to maintain ionic strength constant at 4.00 F where protonation of the malonato complex should be favored.[1,9]

Experimental Section

Materials.—Crude samples of malonatopentaamminecobalt(III) and dimethylmalonatopentaamminecobalt(III) perchlorate salts were prepared as previously described.[5,10] These samples were purified *via* ion-exchange chromatography (Dowex 50W-X2, 200-400 mesh; elution with 2 F $NaClO_4$ separated the desired 2+ band from 3+ impurities) and then were crystallized two times from dilute sodium perchlorate solutions. The purified products exhibited visible absorption spectra typical for this class of compounds[5] (ϵ_{503} 73 M^{-1} cm^{-1}) and the proton magnetic resonance spectra in DMSO-d_6 were completely consistent with the proposed structures (Varian A-60, ambient temperature, CH_2 of malonato

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[1] M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971).

[2] H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969).

[3] (a) T. J. Przystas and A. Haim, *Inorg. Chem.*, **11**, 1017 (1972); (b) J. R. Ward and A. Haim, *J. Amer. Chem. Soc.*, **92**, 475 (1970); (c) A. Haim, *ibid.*, **86**, 2352 (1964).

[4] G. Svatos and H. Taube, *ibid.*, **83**, 4172 (1961).

[5] R. D. Butler and H. Taube, *ibid.*, **87**, 5597 (1965).

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[7] While Taube and Svatos[4] did not identify the supporting electrolyte, their data are consistent with ours if it was sodium perchlorate. Professor H. Taube has kindly communicated to us that the malonato and substituted malonato data of ref 4, and most probably those of ref 5, were obtained in $NaClO_4$ media.

[8] (a) D. L. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2636 (1971); (b) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

[9] E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

[10] D. K. Sebera and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1785 (1961).

at 118 cps downfield from *tert*-butyl alcohol, CH_3 of dimethylmalonato at 4.8 cps downfield from *tert*-butyl alcohol). *Anal.* Calcd for $(NH_3)_5CoOOCCH_2COOH[ClO_4]_2$: C, 8.08; H, 4.07; N, 15.70; Cl, 15.90. Found: C, 8.17; H, 3.97; N, 15.13; Cl, 15.92. Calcd for $(NH_3)_5CoOOCC(CH_3)_2COOH[ClO_4]_2$: C, 12.67; H, 4.68; N, 14.77; Cl, 14.97. Found: C, 12.61; H, 4.51; N, 14.60; Cl, 15.22. (Analyses were performed by Chemalytics, Inc.) Solutions of perchloric acid, sodium perchlorate, lithium perchlorate, and chromium(II) perchlorate were prepared and standardized as previously described.[9]

Methods.—All kinetic runs were performed at 25.0 ± 0.2°, $\mu = 4.00$ *F*, in 5.00-cm cylindrical spectrophotometer cells. They were followed at 500 nm on a Cary Model 14 spectrophotometer equipped with a thermostated cell holder. Anaerobic syringe techniques[9] were used throughout. The initial concentration of cobalt(III) complex was usually about 2.5×10^{-3} *F*, while the initial concentration of chromium(II) was usually about 0.01 *F* for the malonato complex and about 0.05 *F* for the dimethylmalonato complex. Using the standard Los Alamos nonlinear least-squares program,[11] the optical density *vs.* time data were fit to the second-order rate expression

$$\mathrm{OD}_t = \mathrm{OD}_\infty + (\mathrm{OD}_0 - \mathrm{OD}_\infty)\left(\frac{1 - b/a}{1 - (b/a)e^{k(b-a)(t+\theta)}}\right)$$

where the subscript on OD indicates the time of that reading, b and a are the initial concentrations of chromium(II) and cobalt(III), respectively, θ is a time slippage factor to correct for the uncertainty in determining an absolute zero time, and k is the observed second-order rate constant (the reaction is assumed to follow the rate law $k(\mathrm{Co^{III}})(\mathrm{Cr^{II}})$ determined by Svatos and Taube[4]). Within each kinetic run, the calculated OD_t values always fit the observed OD_t's to a standard deviation of less than 0.003 optical density unit and on the average to a standard deviation of less than 0.002 unit. Adjusted values of OD_∞, OD_0, and θ were always within experimental error of the observed values. The individual values of k and their standard deviations determined by this procedure are listed in Table I. All errors quoted in this paper are standard deviations.

TABLE I

RATE CONSTANTS FOR THE CHROMIUM(II) REDUCTION OF MALONATO- AND DIMETHYLMALONATOPENTAAMMINECOBALT(III) AS A FUNCTION OF ACIDITY AND SUPPORTING ELECTROLYTE AT 25° AND $\mu = 4.00$ *F*

	$NaClO_4$		$LiClO_4$	Data from ref 4
(H^+), *F*	k^{obsd}, F^{-1} sec^{-1}	k^{calcd},[a] F^{-1} sec^{-1}	k^{obsd}, F^{-1} sec^{-1}	k^{obsd},[b] F^{-1} sec^{-1}
	Malonato			
1.00	2.64 ± 0.02	2.36	4.15 ± 0.04	2.5
1.00	2.75 ± 0.03	2.36	4.11 ± 0.03	...
2.00	2.75 ± 0.04	2.83	3.90 ± 0.03	2.7
2.00	2.80 ± 0.03	2.83	3.99 ± 0.03	...
3.00	3.28 ± 0.07	3.39	4.25 ± 0.05	...
3.00	3.36 ± 0.06	3.39	3.95 ± 0.05	...
3.95[c]	3.96 ± 0.05	4.03	3.89 ± 0.04	4.0
3.95[c]	3.94 ± 0.04	4.03	4.24 ± 0.04	4.4
	Dimethylmalonato			
1.00	0.242 ± 0.003	0.217	0.325 ± 0.003	...
1.00	0.244 ± 0.003	0.217	...	...
1.90	0.247 ± 0.002	0.247	0.319 ± 0.001	...
1.90	0.254 ± 0.003	0.247	...	...
2.80	0.281 ± 0.003	0.280	0.325 ± 0.002	...
2.80	0.284 ± 0.003	0.280	...	...
3.75[c]	0.322 ± 0.003	0.321	0.310 ± 0.004	...
3.75[c]	0.329 ± 0.003	0.321	...	...

[a] Calculated by the expression $\ln k^{calcd} = \ln 4.03 - 0.181(3.95 - [H^+])$ for malonato and by $\ln k^{calcd} = \ln 0.321 - 0.142(3.75 - [H^+])$ for dimethylmalonato. [b] It is presumed that the original listing of these units as M^{-1} min^{-1} in ref 4 is in error. [c] No supporting electrolyte added.

Results and Discussion

The data in Table I provide no evidence for an acid dependence in the chromium(II) reduction of either malonato- or dimethylmalonatopentaamminecobalt(III) over the range 1–4 *F* $HClO_4$ when lithium perchlorate is used as the supporting electrolyte. The weighted average of the ten malonato rates determined in the presence of lithium perchlorate, or with no electrolyte added, is 4.05 ± 0.14 F^{-1} sec^{-1} and that for the corresponding six dimethylmalonato rates is 0.312 ± 0.007 F^{-1} sec^{-1}. The difference between these two specific rate constants can be rationalized in terms of the greater steric requirements of the dimethylmalonato complex.[1] When sodium perchlorate is used as the supporting electrolyte, both the malonato and dimethylmalonato reactions exhibit an apparent acid dependence which can be accounted for by a change in activity coefficients as H^+ is replaced by Na^+ at constant ionic strength. Newton[8b] has, by assuming that all ions obey Harned's rule,[12] deduced eq 1 to account for this effect

$$\ln k = \ln k^0 + \alpha(\mathrm{H}^+) \qquad (1)$$

where k^0 is the rate constant in pure $NaClO_4$ medium. We have rewritten this expression in the equivalent form

$$\ln k = \ln k^{\mathrm{H}} - \alpha(\mathrm{Na}^+) \qquad (2)$$

where k^{H} is the rate constant in pure $HClO_4$ medium and α has the same value as in eq 1. Using only data obtained at the three highest acidities, plots of ln k^{obsd} *vs.* (Na^+) yield values of α for the malonato and dimethylmalonato reactions of 0.181 ± 0.006 and 0.142 ± 0.007 F^{-1}, respectively. The tabulations of k^{calcd} in Table I were obtained from these values of α, the above listed values of k^{H}, and eq 2. Excellent agreement with k^{obsd} is obtained except at $(H^+) = 1.00$ *F*. Presumably at this acid concentration, in sodium perchlorate, the activity of H^+ has decreased to the point where the inverse acid rate term reported by Svatos and Taube[4] becomes important and thus k^{obsd} is larger than k^{calcd}. The excellent agreement between our malonato $NaClO_4$ data and the data of Svatos and Taube [4] provides strong evidence that their investigation was carried out in sodium perchlorate medium. The $LiClO_4$ data in Table I determine the value of α generated by replacing H^+ by Li^+, at constant ionic strength 4.00 *F*, to be essentially zero for both the malonato and dimethylmalonato reactions (0.001 ± 0.012 and 0.014 ± 0.009, respectively).

In summary, when lithium perchlorate is used as the supporting electrolyte, there is no acid dependence observed for the chromium(II) reduction of either malonato- or dimethylmalonatopentaamminecobalt(III) in the range 1–4 *F* $HClO_4$. When sodium perchlorate is used as the supporting electrolyte, *both* reactions exhibit an acid dependence which may be interpreted as a medium effect. Thus there is no evidence for a special k_h term when malonate functions as a bridging ligand, and the discussions[4-6] based on the existence of such a term must be viewed with reservation.

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Reaction of Bis(tetraethylammonium) Tetrabromodioxouranium(VI) with Liquid Ammonia

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To supplement the somewhat fragmentary information available concerning the ammoniates, amides, and imides of the uranyl ion,[1-3] we have investigated the interaction of $[(C_2H_5)_4N]_2UO_2Br_4$ and anhydrous liquid ammonia. Numerous reactions of the resulting primary and secondary reaction products are also described.

Experimental Section

Unless otherwise indicated, all experimental methods were the same as those reported in recent publications.[4]

Synthesis of $[(C_2H_5)_4N]_2UO_2Br_4$.—This bright yellow salt was prepared in substantially quantitative yield by treatment of a solution of 2.98 g of UO_2Br_2 in 20 ml of 95% ethanol with 3.20 g of $(C_2H_5)_4NBr$ at 25° for 15 min and recrystallized from acetonitrile. *Anal.* Calcd for $[(C_2H_5)_4N]_2UO_2Br_4$: U, 28.0; Br, 37.6. Found: U, 27.8; Br, 37.5.

Interaction of $[(C_2H_5)_4N]_2UO_2Br_4$ and NH_3.—In a typical experiment, 6.01 g of the bromide was treated with 50 ml of liquid ammonia at either −35 or −78° for 15 min. The pale yellow insoluble product was filtered and washed six times[5] with 30 ml portions of ammonia. After drying under reduced pressure for 12 hr, the yield of insoluble product was 3.02 g or 83% based on $[(C_2H_5)_4N]_2UO_2Br_4$. *Anal.* Calcd for $[UO_2(NH_2)_2\cdot NH_3](NH_4Br)_2$: U, 46.2; Br, 31.0; N, 13.6. Found: U, 45.7; Br, 30.9; N, 13.4. Ir data (4000–600 cm^{-1} in all cases): 3270 s, 3215 s, 3160 s, $\sim$1725 br, sh, 1609 ms, $\sim$1595 sh, 1461 w, 1404 ms, 1387 m, 1293 m, 1264 m, 1241 ms, $\sim$1234 sh, 1125 m, $\sim$952 sh, 932 vs, 892 ms, 858 m, 662 m, $\sim$630 sh. Evaporation of the combined supernatant solution and washings provided a pale yellow residue which contained uranium; X-ray diffraction data confirmed the presence of NH_4Br and $(C_2H_5)_4NBr$.

Deammoniation of $[UO_2(NH_2)_2\cdot NH_3](NH_4Br)_2$.—A 2.31 g sample of this product was maintained at 10^{-2} Torr for 3 days, whereupon NH_3 gas was evolved and the intensity of the color of the solid increased. *Anal.* Calcd for $UO_2NH(NH_4Br)_2$: U, 49.5; Br, 33.2; N, 8.7. Found: U, 49.3; Br, 33.2; N, 8.5. Ir data: 3150 ms, 1655 vw, 1599 vw, 1400 ms, 891 ms. An X-ray diffraction pattern showed only lines attributable to NH_4Br.

Uranium(VI) Dioxyimide 2-Ammoniate.—A 2.85 g sample of $UO_2NH(NH_4Br)_2$ was washed 15 times with 20 ml portions of NH_3 at −78° to provide a quantitative yield of a bright orange colored ammonia-insoluble solid. *Anal.* Calcd for $UO_2NH\cdot 2NH_3$: U, 74.6; N, 13.2. Found: U, 74.2; N, 12.9. Ir data: 3325 m, 3200 m, br, 1597 m, 1420 m, br, 1217 m, br, 877 s, br, $\sim$825 sh. This product was amorphous to X-rays. For the white ammonia-soluble product, ir and X-ray diffraction data showed only the presence of NH_4Br.

Pyrolysis of $UO_2NH\cdot 2NH_3$.—Heating a 0.6 g sample at 10^{-2} Torr to and at 200° for 12 hr formed a brown powder that was amorphous to X-rays. *Anal.* Calcd for $UO_2NH\cdot NH_3$: U, 78.8; N, 9.3. Found: U, 78.3; N, 9.2. Ir data: 3330 m, 3200 m, br, 1595 w, 1420 m, br, 890 s, br. Further heating at 330° for 12 hr gave a brown-black powder that did not absorb in the ir. *Anal.* Calcd for U_3O_8: U, 84.8. Found: U, 81.9; N, 0.5. An X-ray diffraction photograph showed only the presence of U_3O_8.

Reactions Using $[UO_2(NH_2)_2\cdot NH_3](NH_4Br)_2$.—Although it was our intention to study certain reactions of uranyl amide, all efforts to remove the associated NH_4Br resulted in decomposition, usually resulting in the formation of the imide. Accordingly, the NH_4Br-containing complex was used to study the following reactions.

With Water.—Exhaustive washing with water at 25° gave a colorless filtrate that contained only NH_4Br and a yellow-orange colored solid that was dried over concentrated H_2SO_4 for 3 days. *Anal.* Calcd for $U_3O_{14}NH_{13}$: U, 74.0. Found: U, 73.8. The X-ray diffraction pattern was the same as that reported earlier[6] for a product empirically formulated as "$3UO_3\cdot NH_3\cdot 5H_2O$."

With Methanol.—Similar treatment with anhydrous methanol gave a clear filtrate and washings that contained only NH_4Br and a yellow Br-free insoluble product. *Anal.* Calcd for $UO_2(OCH_3)_2\cdot CH_3OH$: U, 65.2; C, 9.9; H, 3.0. Found: U, 65.0; C, 9.6; H, 3.2. Ir data: 3302 m, 1036 ms, 1027 ms, 1016 s, 1004 ms, 900 s, 876 m, 810 m.

With Benzoic Acid.—A 0.86 g sample of the mixture was added to 2.5 g of benzoic acid in 20 ml of CH_2Cl_2 at 25° without liberation of NH_3 gas. The yellow insoluble product was washed with CH_2Cl_2, then distilled H_2O, and dried *in vacuo* for 3 days. *Anal.* Calcd for $NH_4[UO_2(C_6H_5CO_2)_3]$: U, 36.5; C, 38.7; H, 2.9; N, 2.2. Found: U, 36.6; C, 38.5; H, 3.0; N, 2.4. The ir spectrum was the same as that reported previously.[7]

With Acetylacetone.—A 1.32 g sample was mixed with 3 ml of acetylacetone in 30 ml of CH_2Cl_2 at 25°. Gaseous NH_3 was liberated, white NH_4Br precipitated, and an orange solution formed. Filtration followed by slow evaporation of the solvent yielded yellow crystals that were recrystallized from CH_2Cl_2 and dried *in vacuo* for 12 hr. *Anal.* Calcd for $UO_2(CH_3COCHCOCH_3)_2\cdot CH_3CNH_2CHCOCH_3$: U, 42.0; C, 31.8; H, 4.1; N, 2.5. Found: U, 42.2; C, 32.1; H, 2.9; N, 3.0. The ir spectrum was essentilly identical with that reported earlier.[8]

Discussion

Following reaction between $[(C_2H_5)_4N]_2UO_2Br_4$ and liquid ammonia, retention of NH_4Br in association with $UO_2(NH_2)_2\cdot NH_3$ persisted despite exhaustive washing and the very high solubility of NH_4Br in NH_3. X-ray diffraction and ir data confirmed the presence of NH_4Br and ν(U–Br) was not observed. The possible alternative formulation, $[UO_2NH\cdot 2NH_3](NH_4Br)_2$, is less attractive since the ir spectrum is more complicated than ordinarily observed for a simple ammine.[9] We therefore assign the band at 1125 cm^{-1} to $\omega(NH_2)$ since this mode was not observed in any of the other compounds isolated and corresponds to the spectrum of $Hg(NH_2)Br$.[10,11] The band at 930 cm^{-1} is assigned to the ν_3 mode of the linear uranyl moiety;[12] the frequency of the ν_1 mode is probably 858 cm^{-1} rather than 892 cm^{-1} since an extensive study of solid uranyl com-

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