difluoride was prepared by standard literature methods. The other reagents were standard shelf items and were used after drying over molecular sieves in the case of liquids and at 150 °C for NaF.

Products were purified by sublimation, trap-to-trap separation, or prolonged exposure to dynamic vacuum. Infrared spectra were obtained by using a liquid film between KBr plates or solids as KBr disks. The ^{19}F and ^1H nuclear magnetic resonance spectra were measured at 60 MHz with CCl_3F and $(CH_3)_4Si$ as internal references. Mass spectra were obtained at 70 eV. Elemental analyses were completed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

In a typical reaction, 5–10 mmol of $CF_3CF_2N{=}SF_2$ and an excess of the amine, diol, or mercaptoethanol at −196 °C were added to a 50-mL Pyrex glass vessel equipped with a Teflon stopcock and containing 30–40 mmol of anhydrous NaF. The vessel was allowed to warm to and remain at room temperature while being stirred magnetically for several days. The product was purified by fractional condensation or, if solid, by sublimation.

New Compounds

$CF_3CF_2N{=}\overline{SN(CH_3)CH_2CH_2N}(CH_3)$. A 62% yield was obtained from the reaction of 8 mmol of $CF_3CF_2NSF_2$ with 18 mmol of $HN(CH_3)CH_2CH_2N(CH_3)H$ (excess NaF). The compound is a sublimable, colorless solid which melts at 59 °C. IR (KBr disk): 2970 (w), 2930 (w), 2895 (m), 2820 (w), 2765 (w), 1650 (s, br), 1528 (w), 1472 (w), 1450 (w), 1372 (m), 1208 (sh), 1193 (s), 1168 (s), 1140 (s), 1100 (m), 1055 (m), 1015 (w), 982 (w), 915 (m), 872 (w), 820 (m), 763 (m), 680 (s), 523 (w), 458 (w) cm^{-1}. Mass spectrum (*m/e*): M^+, 251; $C_2F_5NSN(CH_3)CH_2^+$, 208; M − CF_3^+, 182; $F_2CNSN(CH_3)CH_2^+$, 139; $N\overline{SN(CH_3)CH_2CH_2N}^+$, 117. ^{19}F NMR: $\phi(CF_3)$ −86.4, $\phi(CF_2)$ −75.0. ^1H NMR: $\delta(CH_3)$ 5.8, $\delta(CH_2)$ 7.2. Anal. Calcd: C, 28.76; H, 4.25; N, 16.92. Found: C, 28.69; H, 3.98; N, 16.73.

$CF_3CF_2N{=}\overline{SOCH_2CH_2O}$. A 70% yield was obtained from the reaction of 5.5 mmol of $CF_3CF_2NSF_2$ with 12.6 mmol of $HOCH_2CH_2OH$ (excess NaF). The compound is a slightly volatile, colorless liquid which was purified by fractional distillation. IR (capillary film): 2985 (w), 2920 (w), 1472 (w), 1390 (m), 1265 (vs), 1210 (vs), 1105 (vs), 1025 (sh), 1010 (s), 915 (s), 768 (m), 732 (s), 663 (s), 603 (m), 545 (w), 445 (m) cm^{-1}. Mass spectrum (*m/e*): M^+, 225; M − F^+, 206; $C_2F_5NS^+$, 165; $C_2F_4NSO^+$, 162; $C_2F_5^+$, 119; CF_2NSO^+, 112. ^{19}F NMR: $\phi(CF_3)$ −87.4(t), $\phi(CF_2)$ −83.7 (br), $J_{CF_3-CF_2} = 0.9$ Hz. ^1H NMR $\delta(CH_2)$ 4.5 (mult). Anal. Calcd: C, 21.04; H, 1.76; N, 6.14. Found: C, 21.33; H, 1.78; N, 6.22.

$CF_3\overline{C{=}NSCH_2CH_2O}$. A 15% yield was found from the reaction of 13 mmol of $CF_3CF_2NSF_2$ with 21 mmol of $HOCH_2CH_2SH$ (excess NaF). The compound is a slightly volatile liquid at 22 °C and was separated with great difficulty from the other volatile product, $CF_3C(O)NH_2$ (20% yield), by repeated sublimations. IR (capillary film): 2960 (w), 2910 (w), 1750 (w), 1657 (s), 1467 (w), 1423 (w), 1387 (s), 1337 (s), 1293 (s), 1210 (s), 1145 (s, sh), 1125 (s), 995 (w), 970 (m), 868 (m), 833 (m), 746 (m), 719 (m), 702 (w), 595 (w), 525 (w), 508 (w), 400 (m) cm^{-1}. Mass spectrum (*m/e*): M^+, 171; M − F^+, 152; M − $C_2H_4^+$, 143; $C_4H_2FNS^+$, 115; M − CF_3^+, 102; CF_3CO^+, 97; $OC_2H_4S^+$, 76. ^{19}F NMR: $\phi(CF_3)$ −74.4. ^1H NMR $\delta(CH_2O)$ 4.57 (mult), $\delta(CH_2S)$ 3.17 (mult). Anal. Calcd: C, 28.07; H, 2.42. Found: C, 28.01; H, 2.34.

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Registry No. $CF_3CF_2N{=}\overline{SN(CH_3)CH_2CH_2N}(CH_3)$, 68297-70-1; $CF_3CF_2N{=}\overline{SOCH_2CH_2O}$, 68297-71-2; $CF_3\overline{C{=}NSCH_2CH_2O}$, 68297-72-3; $CF_3CF_2NSF_2$, 4101-37-5; $HN(CH_3)CH_2CH_2N(CH_3)H$, 110--3; $HOCH_2CH_2OH$, 107-21-1; $HOCH_2CH_2SH$, 60-24-2.

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Temperature Dependence of the Photoaquation of Tris(2,2′-bipyridine)chromium(III) Ion in Alkaline Solution[1]

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and Morton Z. Hoffman*[2b]

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Detailed examinations of the thermal[3,4] and photochemical aquation[5] of $Cr(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) in alkaline solution (reaction 1) have led to the conclusion that both

$$Cr(bpy)_3^{3+} \xrightarrow[h\nu,\ kT]{H_2O,\ OH^-} Cr(bpy)_2(OH)_2^+ + bpy \qquad (1)$$

reactions occur via the direct association of the $^4A_2$ ground state or ^2E excited state with H_2O to form the same seven-coordinate intermediate. Evaluation of the rate constant for the thermal reaction at pH 9.8 as a function of temperature (e.g., 4.7×10^{-7} s^{-1} at 11 °C) has resulted in the following activation parameters:[3] $E_a = 22.9 \pm 0.6$ kcal mol^{-1}, $\Delta H_{298}^{\ddagger} = 22.3 \pm 0.6$ kcal mol^{-1}, $\Delta S_{298}^{\ddagger} = -8.8 \pm 1.9$ eu.

Inasmuch as the same seven-coordinate intermediate is believed to be formed from both $^4A_2$ and ^2E electronic states via equivalent reaction paths, $Cr(bpy)_3^{3+}$ offers the unusual opportunity to compare directly the kinetic parameters of ground- and excited-state reactivities of the same species. In this paper we report the temperature dependence of the photochemical aquation of $Cr(bpy)_3^{3+}$ and make such a comparison.

Experimental Section

The $[Cr(bpy)_3](ClO_4)_3\cdot{}^1/_2H_2O$ sample was prepared according to the procedure described previously;[3] however, oxidation was carried out with chlorine gas. All chemicals and solvents used were reagent grade and the water was distilled.

Continuous photolyses were carried out at 313 nm with an Oriel 1000-W Hg-Xe lamp and a 0.25-m Bausch and Lomb grating monochromator (bandwidth 22 nm). To improve the spectral purity of the incident light, the beam was passed through an 8-cm path of cooled distilled water.[6] The intensity of the incident light ($\sim 1 \times 10^{-6}$ einstein min^{-1}) was measured by ferrioxalate actinometry.[7] Constant temperature (±0.1 °C) during irradiation was maintained with a jacketed cell holder and a constant-temperature water bath. Absorption spectra were recorded with an Aminco-Bowman DW-2 spectrophotometer.

Solutions were prepared and handled in dim red light. Quantum yields of bpy release, Φ, were determined in the temperature range 6.3–36.3 °C at pH 9.8 (Britton-Robinson buffer,[8] 0.008 M); the ionic strength was adjusted to 1.0 M with NaCl. Exactly 3.00 mL of $Cr(bpy)_3^{3+}$ ($\sim 1 \times 10^{-3}$ M) solution in a 1-cm quartz cell fitted with a stopcock was deoxygenated with prepurified N_2 for 25 min in the thermostated cell holder and then irradiated at 313 nm for 85–180 s at the desired temperature. A sample of the solution was kept in the dark in the water bath to measure the thermal component of the aquation reaction (2–43% of the total reaction). During irradiation, the solution was stirred with a stream of N_2. Immediately after irradiation, a 2.00-mL aliquot of the irradiated solution was taken for the determination of the concentration of free bpy (±15%) according to the extraction procedure described previously.[3,4] The irradation time was chosen so that no more than 10% of the $Cr(bpy)_3^{3+}$ was photolyzed. Values of Φ represent the average of two to four determinations (standard deviation is ±0.01).

The details of the flash photolysis determination of the decay kinetics of the ^2E state of $Cr(bpy)_3^{3+}$ have been reported.[5]

Results and Discussion

The value of the rate constant of the decay of the ^2E state of $Cr(bpy)_3^{3+}$ (k_0) is pH independent (−0.4 to +13.0)[5] but

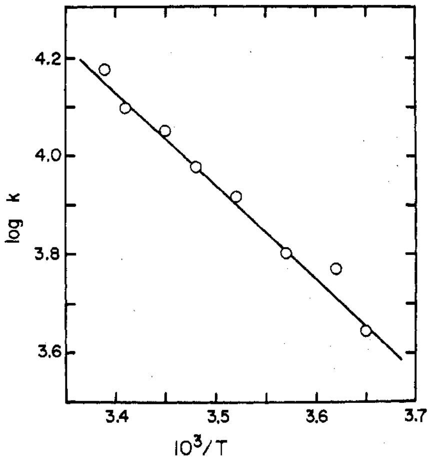

Figure 1. Temperature dependence of the decay of the ^2E state of $Cr(bpy)_3^{3+}$ in a N_2-purged aqueous solution at pH 5.5 (phosphate buffered); transient absorption was monitored at 390 nm.

Table I. Temperature Dependence of the Photochemical Parameters for $Cr(bpy)_3^{3+}$

T, K	Φ^a	$10^{-4} \times k_0,^b$ s^{-1}	$10^{-3} \times k_{rx},^c$ s^{-1}	$10^{-4} \times k_{nr},^d$ s^{-1}
279.5	0.14	0.72	1.0	0.62
284.3	0.15	0.93	1.4	0.79
295.3	0.18	1.6	2.9	1.3
301.0	0.20	2.1	4.3	1.7
305.8	0.19	2.6	5.0	2.1
309.5	0.19	3.1	5.9	2.5

[a] Measured at pH 9.8 in N_2-purged solution (see text). [b] Interpolated from the data in Figure 1. [c] $k_{rx} = \Phi k_0$. [d] $k_{nr} = k_0 - k_{rx}$.

varies with temperature as shown in Figure 1 giving $E_a = 8.3 \pm 0.1$ kcal mol^{-1}. The same values of the kinetic parameters of the decay of ^2E are obtained from phosphorescence intensity and lifetime measurements.[5] The values of Φ as a function of temperature are given in Table I.

The direct association of the $^4A_2$ ground state of $Cr(bpy)_3^{3+}$ with H_2O is represented by equilibrium reaction 2; the corresponding association of the ^2E excited state with H_2O is given in reaction 3 which competes with radiative and nonradiative decay (reactions 4 and 5). Deprotonation of the seven-coordinate intermediate at pH >8 and further interaction with either H_2O or OH^- leads rapidly, irreversibly, and quantitatively to the final aquation product (reaction 6). Therefore,

$$(^4A_2)Cr(bpy)_3^{3+} + H_2O \underset{k_{-th}}{\overset{k_{th}}{\rightleftharpoons}} Cr(bpy)_3(H_2O)^{3+} \quad (2)$$

$$(^2E)Cr(bpy)_3^{3+} + H_2O \xrightarrow{k_{rx}} Cr(bpy)_3(H_2O)^{3+} \quad (3)$$

$$(^2E)Cr(bpy)_3^{3+} \xrightarrow{k_{rad}} (^4A_2)Cr(bpy)_3^{3+} + h\nu \quad (4)$$

$$(^2E)Cr(bpy)_3^{3+} \xrightarrow{k_{nr}} (^4A_2)Cr(bpy)_3^{3+} \text{ (non-radiative)} \quad (5)$$

$$Cr(bpy)_3(H_2O)^{3+} \overset{-H^+}{\rightleftharpoons} Cr(bpy)_3(OH)^{2+} \xrightarrow{H_2O,\ OH^-} Cr(bpy)_2(OH_2)_2^{+} + bpy \quad (6)$$

in mildly alkaline solution (pH <11), the rate constant and activation parameters of the overall thermal reaction reflect the values for the slow, rate-determining step, k_{th}. The value of k_{-th} has been estimated from flash photolysis data[5] to be ≤ 10 s^{-1} so that the reverse of reaction 2 can be ignored compared with the rapid deprotonation of $Cr(bpy)_3(H_2O)^{3+}$ in alkaline solution. Direct attack of OH^- on the ground state complex[4] does not become kinetically important until pH 11. Similarly, OH^- does not competively quench the ^2E state[5] until pH 13.

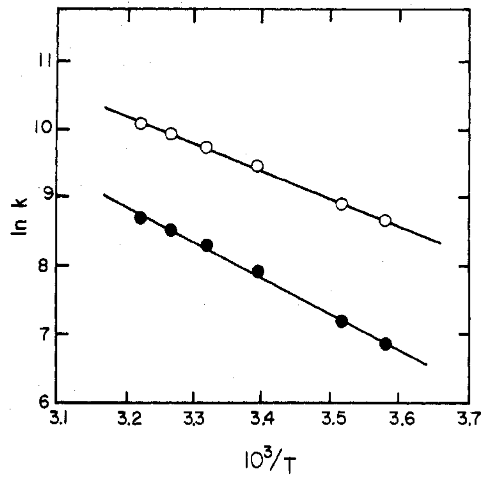

Figure 2. Temperature dependence of k_{nr} (○) and k_{rx} (●).

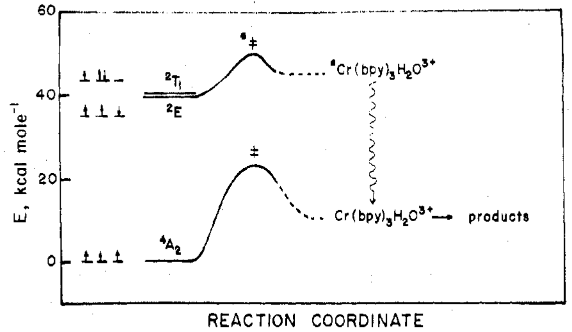

Figure 3. Profiles for the reaction of the $^4A_2$ ground state and the lowest doublet excited states of $Cr(bpy)_3^{3+}$ with H_2O. The electron configurations shown are for the occupied t_{2g} orbitals of $Cr(bpy)_3^{3+}$ assuming octahedral microsymmetry.

Excitation of $Cr(bpy)_3^{3+}$ into the manifold of spin-allowed excited states leads to quantitative formation of the $^4T_2$ state.[5] Inasmuch as the $^4T_2 \rightarrow {}^2E$ intersystem crossing efficiency[9] is ~ 1, the quantum yield of formation of ^2E is ~ 1. The rate constant for the decay of ^2E according to reactions 3–5 is given by the expression $k_0 = k_{rx} + k_{rad} + k_{nr}$. The quantum yield of the ith process involving ^2E is given as $\Phi_i = k_i/k_0$. Because $\Phi_{rad} < 10^{-3}$, $k_{rad} < k_{rx} + k_{nr}$ and can be ignored in the k_0 expression.[5,10] Further, because reaction 6 is quantitative in alkaline solution, the overall quantum yield of photoaquation, Φ, can be identified as Φ_{rx}. Thus, $k_{rx} = \Phi k_0$ and $k_{nr} = k_0 - k_{rx}$. Values of k_0 are interpolated from the data in Figure 1 and are given in Table I together with values of k_{rx} and k_{nr} as a function of temperature. Arrhenius plots of k_{rx} and k_{nr} are shown in Figure 2 from which values of $E_a(rx) = 10.2 \pm 0.4$ kcal mol^{-1} and $E_a(nr) = 7.9 \pm 0.1$ kcal mol^{-1} are obtained. The linear plot of ln (k_{rx}/T) vs. $1/T$ yields $\Delta H^{*}_{rx} = 9.6 \pm 0.4$ kcal mol^{-1} and $\Delta S^{*}_{rx} = -10.0 \pm 1.4$ eu.

Comparison of the kinetic parameters for the reactions of the $^4A_2$ and ^2E species with H_2O to form the seven-coordinate intermediate shows that the excited-state reaction is $\sim 10^{10}$ times faster, requires considerably less enthalpy for activation, and exhibits about the same entropy lowering in going to the activated complex than does the thermal reaction. In order to rationalize these comparisons, consideration is given to the profiles of the reactions (Figure 3). The ^2E state lies 39 kcal mol^{-1} above the $^4A_2$ ground state and is in thermal equilibrium with the $^2T_1$ state (1.7 kcal mol^{-1} separation).[11] Inasmuch as the ^2E and $^4A_2$ states have identical geometries, there being no Stokes shift between the $^2E \leftrightarrow {}^4A_2$ emission[11] and absorption[12] bands, it can be assumed that the activated complexes from these states also have the same geometries. It is a condition of the transition-state theory[13] that reactants and activated complex be in equilibrium. Therefore, the activated complex from ^2E must be in a state of electronic excitation ($*\ddagger$) while that from $^4A_2$ is in the ground state ($\ddagger$). As a first approximation, we assume that the spin multiplicities of the activated complexes are the same as the reactants from which they derive. Passage of the system from $*\ddagger$ to the seven-coordinate intermediate would proceed through an excited-state species ($^*Cr(bpy)_3(H_2O)^{3+}$) which, via a nonradiative process, converts to $Cr(bpy)_3(H_2O)^{3+}$. The exact energetics of the seven-coordinate species are, of course, unknown but their values have no effect on the activation parameters.

Both activated complexes can be assumed to show incipient formation of the Cr–O bond and the distortion and loosening of the normally regular structure of the bpy ligands in order to accommodate the incoming H_2O. The values of $\Delta H^{\ddagger}$ for both the ^2E and $^4A_2$ reactions then reflect the energy expended to loosen the six Cr–N bonds (although certainly not all to the same extent) in balance with energy gained from the formation of the Cr–O bond. The negative values of $\Delta S^{\ddagger}$ imply that the coalescence of the two microscopic particles is the dominant contributor to the entropy of activation and is the same for both the thermal and photochemical reactive paths.

Because of the geometric similarities between $^4A_2$ and ^2E, $\Delta H^{\ddagger}$ for the associative reaction from both states would be expected to be the same. However, $\Delta H^{\ddagger}$ of the reaction from ^2E is found to be $\sim$13 kcal mol^{-1} less than the comparable reaction from $^4A_2$. Recently we proposed[14] that the reaction of ^2E arises from the interaction of the solvent with the thermally equilibrated $^2T_1$ state which has a vacant t_{2g} orbital[15] available to accommodate the Lewis base solvent molecule oriented between the bidentate bpy ligands. Although the $^2T_1$ state has a $t_{2g}{}^3$ configuration and a geometry similar to that of ^2E and $^4A_2$, the vacant t_{2g} orbital[15] would result in less reorganizational energy being required to form the activated complex and a value of $\Delta H^{\ddagger}$ smaller than that obtained from the reaction of $^4A_2$. The factor of 10^{10} difference in the values of k_{th} and k_{rx} simply reflects these differences in $\Delta H^{\ddagger}$.

Because the nonradiative decay of ^2E is an intramolecular process involving the transformation of metal-centered electronic energy to ligand-centered vibrational energy,[17] the value of E_a(nr) cannot be applied to a simple model. Nonradiative processes usually have rather low temperature coefficients;[18] there does not appear to be sufficient data available for nonradiative processes in coordination complexes to make any further quantitative analysis.

Acknowledgment. The authors thank Professor V. Balzani and his associates for their continued interest in this work.

Registry No. $Cr(bpy)_3{}^{3+}$, 15276-15-0.

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(1) Research supported by the National Research Council of Canada (Grant No. A-5443), the National Science Foundation (Grant No. CHE 76-21050), and the North Atlantic Treaty Organization (Grant No. 658).
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Additions and Corrections

1978, Volume 17

Kenneth R. Seddon* and Valerie H. Thomas: Tetrachlorophosphonium Oxotetrachlorochromate(V).

Page 750. In the Experimental Section under preparation i the first sentence should read: A solution of phosphorus pentachloride (2 g) in phosphorus oxide trichloride (70 cm^3) was added slowly to a solution of chromium(VI) dioxide dichloride (0.8 cm^3) in phosphorus oxide trichloride (5 cm^3).—K. R. Seddon

R. W. Braun, A. H. Cowley,* M. C. Cushner, and R. J. Lagow*: (Trifluoromethyl)sulfur Trifluoride. An Improved Synthesis, New NMR Data, and Stereochemistry.

Page 1680. The axially substituted trigonal-bipyramidal structure, **1**, should be

—A. H. Cowley