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 ~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.

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

References and Notes

(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

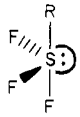
1978, Volume 17

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