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Contribution from the Departments of Chemistry, Stanford University, Stanford, California 94305,
and Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

Enthalpy of Formation of Nitrosylpentaammineruthenium(II) from $NO^+(aq)$ and Aquopentaammineruthenium(II)

James F. Wishart,[†] Henry Taube,*[†] Kenneth J. Breslauer,[‡] and Stephan S. Isied[‡]

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An estimate of the enthalpy change associated with the substitution of H_2O in $(NH_3)_5RuOH_2^{2+}$ by $NO^+(aq)$ has been made by thermochemical measurements on a cycle of reactions, which includes the reaction of $(NH_3)_5RuOH_2^{2+}$ with $NO_2^-(aq)$ and which involves the assumption that the heat of dissolution of $NOBF_4(s)$ to produce $NO^+(aq) + BF_4^-(aq)$ is close to the heat of dissolution of $CsBF_4(s)$. The chemistry is complicated because the reaction of $(NH_3)_5RuOH_2^{2+}$ with NO_2^- ultimately produces *trans*-$[(NH_3)_4Ru(OH)NO]^{2+}(aq)$ rather than $[(NH_3)_5RuNO]^{3+}$. Reasonably good estimates of the enthalpy changes of the reactions needed for the cycle to close on $[(NH_3)_5RuNO]^{3+}$ can be made, and when these are combined with the experimental results, they yield as ΔH° for the reaction of interest -52 kcal mol^{-1}. We believe that this result is accurate to within 5 kcal, and the conclusion that the reaction of $NO^+(aq)$ with Ru(II) is more exothermic than that of the isoelectronic CO(aq) (-38.2 ± 1.2 kcal mol^{-1}) seems safe. The assumption as to the heat of solution of $NOBF_4(s)$ and $CsBF_4(s)$ is validated by the finding that the enthalpy change for the formation of $2H^+ + NO_2^-$ by the reaction of $NO^+(aq)$ with water, -10.6 ± 0.5 kcal mol^{-1}, which can be calculated from our results, lies between upper and lower limits set by the work of others.

Introduction

Previous work[1,2] has shown that the enthalpies of substitution of H_2O by $N_2(aq)$ and CO(aq) in $[(NH_3)_5RuOH_2]^{2+}$ are -9.8 ± 1.8 and -38.2 ± 1.4 kcal mol^{-1}, respectively. To extend this series of isoelectronic ligands, we undertook the determination of the corresponding enthalpy for the $NO^+(aq)$ ion. The nitrosyl cation is very unstable in the presence of water, reacting rapidly as follows:

$$NO^+ + H_2O \rightarrow 2H^+ + NO_2^- \qquad (1)$$

(The products are $HNO_2 + H^+$ in more concentrated solution.) The nitrosyl cation is well characterized in salts. Consequently, thermochemical measurements with the cation can be made with a nitrosonium salt as a reagent. The results of such measurements, however, are not directly comparable to those which have been obtained for $N_2(aq)$ and CO(aq). To make comparison possible, we have introduced the assumption that the heat of dissolution of $NOBF_4(s)$

$$NOBF_4(s) \rightarrow NO^+(aq) + BF_4^-(aq)$$

would be the same as that of $CsBF_4(s)$

$$CsBF_4(s) \rightarrow Cs^+(aq) + BF_4^-(aq)$$

and, as part of this study, we have measured the enthalpy change for the latter reaction. We justify our assumption on the basis that the radius of Cs^+ (1.67 Å)[3] is very near the mean radius of NO^+ (1.68 Å).[4] However, the unit cell dimensions for $NOClO_4$ are closer to those of $RbClO_4$ than of $CsClO_4$,[7] and in retrospect, we think that $RbBF_4$ or KBF_4 would have been a better choice than $CsBF_4$ as a substitute for $NOBF_4$. It should be noted, however, that any error arising from our choice is likely to be small since the heats of solution are not likely to be much different. Specifically, the heats of solution[8] of $CsClO_4$, $RbClO_4$, and $KClO_4$ are 13.25, 13.56, and 12.2 kcal mol^{-1}, respectively.[8]

Experimental Section

The preparation and handling of the solutions of $[(NH_3)_5RuOH_2]^{2+}$ have been described elsewhere.[1] Nitrosyl tetrafluoroborate, as purchased from Alfa Products, was used as the source of NO^+. The reaction medium for each calorimetric experiment was $HTHAM^+$/THAM buffer (0.075 M/0.025 M, pH 8.0 THAM = tris(hydroxyethyl)aminomethane) in 0.10 M sodium *p*-toluenesulfonate (Na(tos)). The ionic strength was ca. 0.18 M except for the experiment on the reaction of $(NH_3)_5RuOH_2^{2+}$ with NO_2^-, where it was 0.23 M. After the two reagent solutions were mixed, the concentration of Ru(II) was 3.4×10^{-3} M and the concentration of NO_2^- was 0.05 M. A correction was applied for the integral heat of dilution of $NaNO_2$. The heat of solution of $CsBF_4$ was measured in 0.10 M Na(tos) solution without THAM buffer.

The measurements of the heat of solution of $CsBF_4(s)$ and the heat of reaction of $NOBF_4(s)$ with water were performed in a solution calorimeter,[9] consisting of a mechanically stirred Dewar flask containing 180 mL of solution. The temperature was monitored by an immersed thermistor, and the heat capacity was determined for each experiment by electrical calibration using a standard resistance. The solid sample was introduced via a disposable plastic syringe from which the delivery end had been removed. The compound was retained within the syringe by a round plug of sheet rubber cut to fit the inside diameter of the syringe. Pushing the plunger of the syringe expelled the plug and compound into the solution, initiating the reaction. For the experiments involving $NOBF_4$ the syringes were filled under an atmosphere of dry N_2.

Results

As noted above, ΔH° for reaction 1 cannot be measured directly. We can calculate its value by adding the enthalpy values for reactions 2–4. The ΔH° values (kcal mol^{-1}) for each reaction

$$NOBF_4(s) + 2THAM(aq) + H_2O \rightarrow 2HTHAM^+(aq) + NO_2^-(aq) + BF_4^-(aq) \quad [-21.8 \pm 0.5] \quad (2)$$

$$NO^+(aq) + BF_4^-(aq) + NOBF_4(s) \quad [-11.5 \pm 0.1] \quad (3)$$

$$2HTHAM^+(aq) \rightarrow 2H^+(aq) + 2THAM(aq) \quad [+22.7] \quad (4)$$

$$\text{net:} \quad NO^+(aq) + H_2O \rightarrow 2H^+(aq) + NO_2^-(aq) \quad [-10.6 \pm 0.5] \quad (1)$$

are shown in brackets. For reactions 2 and 3, the ΔH° values were determined in the present work (as mentioned in the Introduction, $CsBF_4(s)$ was used as a stand-in for $NOBF_4(s)$ in

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[†] Stanford University.
[‡] Rutgers University.

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(3) *CRC Handbook of Chemistry and Physics*, 55th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1974; p F-198.

(4) The interatomic distance in NO^+ is 1.06 Å.[5] The van der Waals radii of N and O are 1.55 and 1.50 Å,[6] respectively. Therefore, the long axis of NO^+ is 4.11 Å and the short axis about 3.05 Å. The geometric mean of the radii is $(1.52 \times 1.52 \times 2.055)^{1/3} = 1.68$ Å.

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reaction 3) while, for reaction 4, $\Delta H°$ was obtained from the literature.[10] As shown, the net reaction of interest (reaction 1) is exothermic by 10.6 kcal mol^{-1}.

The reaction

$$[(NH_3)_5RuOH_2]^{2+} + NO_2^- + H_2O \rightarrow [(NH_3)_5RuNO]^{3+} + 2OH^- \quad (5a)$$

has been reported[11] to take place readily, and we have made use of this result in our work. Under our conditions, however (buffer at pH 8.0), the reaction product is *trans*-$[(NH_3)_4Ru(OH)NO]^{2+}$, so that the net change in the calorimetric experiment is

$$[(NH_3)_5RuOH_2]^{2+}(aq) + NO_2^-(aq) + 2HTHAM^+(aq) \rightarrow \textit{trans}\text{-}[(NH_3)_4Ru(OH)NO]^{2+}(aq) + 2THAM(aq) + NH_4^+(aq) + H_2O(l) \quad [-21.0\ \text{kcal mol}^{-1}] \quad (5b)$$

The identity of the product was confirmed by the N–O infrared stretching frequency of 1842 cm^{-1} found for the bromide salt recovered from a reaction mixture. Pell and Armor[12] report 1845 cm^{-1} for the same compound but 1913 cm^{-1} for $[(NH_3)_5RuNO]Br_3$. The production of the hydroxo product is not surprising in view of the reported conversion of $[(NH_3)_5RuNO]^{3+}$ to *trans*-$[(NH_3)_4Ru(OH)NO]^{2+}$ in aqueous ammonia.[11]

The enthalpy measurements for reaction 5b were complicated by decomposition of the $[(NH_3)_5RuOH_2]^{2+}$ reagent solution, which resulted in the formation of a black precipitate. The reactions were found to become increasingly exothermic as time elapsed. The reported value of $\Delta H°$ was obtained by extrapolating data for four successive runs to zero time. Ruthenium(II) ammines are unstable with respect to disproportionation to Ru(s) and to a higher oxidation state, and the reaction is apparently catalyzed by Ru(s).

When reaction 5b is combined with reactions 2 and 3, the result is

$$[(NH_3)_5RuOH_2]^{2+}(aq) + NO^+(aq) \rightarrow \textit{trans}\text{-}[(NH_3)_4Ru(OH)NO]^{2+}(aq) + NH_4^+ \quad [-54\ \text{kcal mol}^{-1}] \quad (6)$$

Discussion

Nitrosyl Ion. The enthalpy change reported for reaction 1 depends on the assumption that the heats of solution of $CsBF_4$(s) and $NOBF_4$(s) are the same to a reasonable degree of accuracy. To test this assumption, the enthalpy for reaction 1 obtained in this work will be compared to other thermodynamic observations that have been made on the same reaction.

Seel and Schwaebel[13] studied the kinetics of the reaction

$$NO_2^-(aq) + N_3^-(aq) + 2H^+(aq) \rightarrow N_2 + N_2O + H_2O(l) \quad (7)$$

and found the rate law to be

$$\text{rate} = k[H^+]^2[NO_2^-]$$

with $\Delta H^‡ = +12.8$ kcal mol^{-1}, $\Delta S^‡ = +12$ cal deg^{-1} mol^{-1}, and $\Delta G^‡ = +9.2$ kcal mol^{-1}.

Evidence from this and other systems[14] indicates that the rate-determining step is represented by the reverse of reaction 1. Since $\Delta H^‡ > \Delta H°$, +12.8 kcal mol^{-1} is the upper limit of the enthalpy for the reverse of reaction 1.

Bayliss et al.[15] determined the equilibrium quotient ($K_{eq} = 3.0 \times 10^{-7}$) for the reaction

$$H^+(aq) + HNO_2(aq) \rightarrow NO^+(aq) + H_2O(l) \quad (8)$$

From K_{eq}, we calculate $\Delta G° = +8.9$ kcal mol^{-1}, and since $\Delta S°$ is expected to be greater than zero for a reaction of this type, we expect $\Delta H° > \Delta G°$, so $\Delta H°_{H^+,HNO_2} > +8.9$ kcal mol^{-1}. The enthalpy of protonation of nitrite ion has been reported by Latimer[16] as +3.0 kcal mol^{-1}. When this is taken into account, the lower limit of $\Delta H°$ for the reverse of reaction 1 is +5.9 kcal mol^{-1}.

Our indirectly determined enthalpy of $+10.6 \pm 0.5$ kcal mol^{-1} for the reverse of reaction 1 lies within the limits established by other experiments:

$$+5.9 < \Delta H° < +12.8\ \text{kcal mol}^{-1}$$

It has been inferred that the activation energy for the reaction of NO^+(aq) with nucleophiles is quite small,[14] and our value of $\Delta H°$, close to the upper limit of +12.8 kcal, is consonant with this interference.

Enthalpy of Substitution of Nitrosyl Ion onto $[(NH_3)_5RuOH_2]^{2+}$. For purposes of comparison with the enthalpies of substitution of dinitrogen and carbon monoxide, the enthalpy change for reaction 6 must be corrected by the enthalpies of reactions 9–11.

$$[(NH_3)_5RuOH_2]^{2+} + NO^+(aq) \rightarrow \textit{trans}\text{-}[(NH_3)_4Ru(OH)NO]^{2+} + NH_4^+ \quad (6)$$

$$NH_4^+(aq) \rightarrow NH_3(aq) + H^+(aq) \quad (9)$$

$$[(NH_3)_4Ru(OH)NO]^{2+} + H^+(aq) \rightarrow [(NH_3)_4Ru(H_2O)NO]^{3+} \quad (10)$$

$$[(NH_3)_4Ru(H_2O)NO]^{3+} + NH_3(aq) \rightarrow [(NH_3)_5RuNO]^{3+} + H_2O(l) \quad (11)$$

$$\text{net:}\quad [(NH_3)_5RuOH_2]^{2+} + NO^+(aq) \rightarrow [(NH_3)_5RuNO]^{3+} + H_2O(l) \quad (12)$$

The enthalpy of reaction 9 has been reported[17] as +12.4 kcal mol^{-1}. Values of $\Delta H°$ for reactions 10 and 11 are not known. That of reaction 11 can be estimated from the free energies of substitution of NH_3 onto $[(NH_3)_5RuOH_2]^{2+}$ and $[(NH_3)_5RuOH_2]^{3+}$ (−6.2[18] and −6.6[19] kcal mol^{-1}, respectively). Evidence from the association of NH_3 with Ni^{2+}(aq) ($\Delta S = -0.41$ cal deg^{-1} mol^{-1})[20] indicates that ΔS for the similar reactions discussed here would be negative and close to zero. We therefore estimate ΔH for reaction 11 to be about −6.5 kcal mol^{-1}. An estimate for the enthalpy of reaction 10 can be made from the pK_a of H_2O in $[(NH_3)_4Ru(H_2O)NO]^{3+}$, which has been measured[21] as 1.4 and corresponds to a free energy of −1.9 kcal mol^{-1} for reaction 10. If the entropy change in reaction 10 is similar to that obtained for the reaction $[(NH_3)_5Ru(pyz)]^{2+} + H^+(aq) \rightarrow [(NH_3)Ru(pyzH)]^{3+}$ ($\Delta S = -5.1$ cal mol^{-1} deg^{-1}), which has similar charge types, the enthalpy of reaction 10 would be about −3.4 kcal mol^{-1}. If the true value of $-\Delta S$ is larger than that assumed here, ΔH would be more negative than −3.4 kcal mol^{-1}.

Summing the observed and estimated enthalpies for reactions 6, 9, 10, and 11, we obtain an overall enthalpy estimate for reaction 12 of −52 kcal mol^{-1}. Despite the uncertainties inherent in the

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arguments presented above, we are reasonably confident that the enthalpy of reaction 12 is close to −50 kcal mol^{-1}. This enthalpy for substitution of NO^+(aq) onto $[(NH_3)_5RuOH_2]^{2+}$ is much more exothermic than the corresponding −38.2 ± 1.4 kcal mol^{-1} for CO(aq) as a ligand. Such a large exothermicity is consistent with the view that when NO^+ combines with $(NH_3)_5RuOH_2{}^{2+}$, there is an enormous redistribution of electronic charge. The high acidities of $[(NH_3)_4Ru(NO)OH_2]^{2+}$ ($pK_a = 4.1$ and 1.4 for cis and trans forms,[21] especially in the case of the trans isomer, which is even more acidic than $[(NH_3)_5RuOH_2]^{3+}$ ($pK_a = 4.1$)[22] suggests that the nitrosyl group bears a net negative charge in this case.

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Registry No. $[(NH_3)_5RuNO]^{3+}$, 37874-79-6; $[(NH_3)_5RuOH_2]^{2+}$, 21393-88-4; NO^+, 14452-93-8.

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Contribution from the School of Chemistry,
University of Sydney, Sydney, NSW 2006, Australia

Partial Molal Volumes of Spin-Equilibrium Metal Complexes

Robert A. Binstead and James K. Beattie*

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The partial molal volumes of spin-equilibrium complexes of iron(II), iron(III), and cobalt(II) have been measured and compared with known crystal volumes. In each case close agreement within several cubic centimeters per mole is found, indicating that crystal packing and solvation contacts are similar. The volume difference between the high-spin and low-spin isomers of the iron complexes was obtained previously by ultrasonic absorption measurements and for the cobalt complex is calculated from the temperature dependence of the magnetic moment and the electronic absorption spectrum and the pressure dependence of the absorption spectrum. The difference in the complex ion radii is calculated and a minimum value obtained for the change in the metal–ligand bond lengths between the spin isomers. By a comparison of these with differences observed in crystal structures, an indication of the solvation of the complexes is obtained.

Introduction

The partial molal volumes of many ions have been determined,[1] but there are few measurements for metal complexes.[2] The necessary data are obtained from precise measurements of the densities of solutions of the complexes as a function of concentration, measurements which are considerably simplified with currently available commercial technology. We have made such measurements in conjunction with ultrasonic relaxation studies of the dynamics of the spin equilibrium that exists in some metal complexes between low-spin and high-spin d-electron configurations.[3-5] The transition from the low-spin to the high-spin state results in lengthening of the metal–ligand bonds and a consequent increase in the volume of the complex. The magnitude of the volume change can be obtained from the amplitude of the ultrasonic absorption.

The change in the metal complex radius accompanying the spin-state transition can be calculated from the partial molal volume and the volume difference between the spin isomers. Comparisons can then be made with known bond length differences obtained from crystal structures. In this paper we report results for four spin-equilibrium complexes for which all of the necessary data are available.

Experimental Section

The iron compounds were prepared as described previously.[3-5] Bis(terpyridine)cobalt(II) chloride dihydrate was prepared by adding dropwise a solution of 2.38 g (10 mmol) of $CoCl_2 \cdot 6H_2O$ in 40 mL of distilled water to a stirred suspension of 5.00 g (21.4 mmol) of terpyridine in 75 mL of distilled water. The resulting dark brown reaction mixture was stirred for 45 min and then filtered to remove excess terpyridine and a trace of the green impurity, $[Co(terpy)Cl_2]$.[6] The solution was concentrated to 35 mL by rotary evaporation and filtered again, removing a further trace of terpyridine but no further green impurity, and then taken to dryness by rotary evaporation. The brown solid was dissolved in a minimum volume of methanol and filtered to remove any trace of green impurity (none was detected), and the filtrate was taken to dryness by rotary evaporation. The purified brown solid was dissolved in a minimum volume of water and filtered and the solution concentrated to 20 mL by rotary evaporation. After the solution was cooked in an ice bath, the dark brown crystals that were formed were collected by filtration, air-dried, and then dried for 48 h in vacuum at room temperature over P_2O_5. The brown crystalline product was free of any green impurity and gave satisfactory elemental analyses.

Density difference measurements were made by using an Anton Parr (Graz, Austria) DMA-02C precision density meter. The temperature of 25.0 °C was maintained by using a locally constructed precision temperature bath controlled to ±0.0005 °C with a Bayley Instruments Co. (Danville, CA) Model 121 precision temperature controller. With the room temperature controlled to 25.0 ± 0.5 °C by air conditioning, temperature fluctuations of ±0.01 °C were obtained in the density meter, resulting in density difference measurements precise to $\pm 3 \times 10^{-6}$ g cm^{-3} for aqueous solutions and to $\pm 3 \times 10^{-5}$ g cm^{-3} for tetrahydrofuran solutions.

From the density difference measurements the apparent molal volume (Φ_V) of the solutes were calculated by using eq 1, where m is the molal

$$\Phi_V = \frac{1000}{m d_0 d_s}(d_0 - d_s) + \frac{MW}{d_s} \tag{1}$$

concentration, d_s and d_0 are the densities of the solution and solvent, respectively, and MW is the molecular weight of the solute.[1] The partial molal volume of the solute, $\bar{V}^\circ_s$, is determined from the concentration dependence of the apparent molal volume by extrapolating Φ_V to infinite dilution where Φ°_V is equal to $\bar{V}^\circ_s$.

Variable-temperature electronic spectra were recorded with a Varian Techtron Model 635 spectrophotometer and jacketed quartz cells in conjunction with a Colora WK-5 refrigerated constant-temperature bath. The data were corrected for changes in solvent density, and hence sample concentration, with temperature.[7]

Variable pressure electronic spectral measurements were obtained at the University of Melbourne on a Varian Techtron 635D spectrophotometer fitted with a thermostated, high-pressure cell in the sample beam.[8,9] Single-wavelength absorbance measurements were recorded at

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