$$cis\text{-}[Co(en)_2(NHR_2)Br]^{2+} + OH^- \longrightarrow [Co(en)_2(NHR_2)OH]^{2+} + Br^-$$

(where NHR_2 = $NH_2CH_2CH_2Br$, $NH_2CH_2CH_2OH$, or C_2H_4NH) are the same, $k_{obsd} = k_{Br}[OH^-]$, and the second-order rate constants (k_{Br}) are similar, Table VII. Both sets of results are consistent with the SN1CB mechanism proposed for basic hydrolysis of acido cobalt(III) complexes.[14] Also, hydrolysis of the bromo monodentate ethanolamine complex in the presence of N_3^- ion leads to chelated ethanolamine, hydroxoethanolamine, and azidoethanolamine products, presumably by competition for the five-coordinate deprotonated intermediate by the coordinated nucleophile, water, and N_3^-. While similar competitive characteristics are shown during the hydrolysis of related complexes,[11] a novel feature in the present instance is the intervention of the coordinated nucleophile; this aspect of the study may lead to some interesting synthetic possibilities and to a more sensitive way of looking at competition during the base hydrolysis of cobalt(III) complexes.

All three *cis*-bromo complexes gave largely *cis*-hydroxo or tris-chelate products in somewhat larger amounts (~86%) then for the *cis*-$[Co(en)_2NH_3Br]^{2+}$ analog under the same conditions (77%). Also partial retention (~50%) of optical activity was observed, which agrees with previous observations.[11] However, these aspects need to be examined more closely under carefully controlled conditions, and the experiments will be repeated in detail in connection with other studies relating to the mechanism of the base hydrolysis reaction.

Concluding Remarks. The advantages of coordinated nucleophiles to effect organic reactions appear to be several. They seem to be extraordinarily efficient even though their basicity is reduced by a factor of at least 10^6–10^8 on coordination to Co(III). In this way substitution rates are enhanced over the intermolecular process by at least a factor of 10^4, and possibly by as much as 10^{12}.[24] Also the metal may function as a protecting group for sensitive areas in the coordinated molecule, and since the complex moiety is asymmetric it may direct the organic synthesis to give a stereospecific product. Recovery of the organic species is readily achieved through reduction of Co(III) to the labile Co(II) complex in acid solution. Coordinated OH^- could also be useful for hydrolysis of ligands sensitive to base in regions other than the reacting site, since the rate of the intramolecular reaction is likely to be independent of hydroxide ion at a pH >6. Finally, the reactions discussed in this paper offer interesting possibilities for the synthesis of chelate complexes. For example, using a sufficiently acidic *cis*-amine group, coordinated 2-bromoethylamine might be expected to chelate rather than cyclize internally to ethylenimine. In this way stereoisomers of multidentate ligands might by stereospecifically synthesized. Similarly, nucleophiles other than N and O should also be effective.

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Equilibria and Rates in the Formation of $[Ru(NH_3)_5N_2]^{2+}$ and $[(Ru(NH_3)_5)_2N_2]^{4+}$

J. N. Armor and H. Taube*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received May 4, 1970*

Abstract: The equilibrium constant K_1 for the reaction $Ru(NH_3)_5OH_2^{2+} + N_2(aq) = Ru(NH_3)_5N_2^{2+} + H_2O(liq)$ has been measured both by a static and a kinetic method. K_1 at 25° is 3.3×10^4, and $\Delta H_1°$ and $\Delta S_1°$ by the static and kinetic methods, respectively, are -10.1 ± 1.4, -9.4 ± 0.9 kcal/mol and -13 ± 5, -10 ± 3 eu. The equilibrium constant K_2 for the reaction $Ru(NH_3)_5OH_2^{2+} + Ru(NH_3)_5N_2^{2+} = [Ru(NH_3)_5N_2Ru(NH_3)_5]^{4+} + H_2O(liq)$ has been measured by a static method. At 25° and $\mu = 0.10$, $K_2 = 7.3 \times 10^3$, $\Delta H_2° = -11.2 \pm 1.4$ kcal/mol, and $\Delta S_2° = -20 \pm 5$ eu. The rate constant k_1 for the formation of $Ru(NH_3)_5N_2^{2+}$ is $7.3 \times 10^{-2}\ M^{-1}\ sec^{-1}$, in good agreement with published measurements, $\Delta H_1^{\ddagger} = 18.3 \pm 0.3$ kcal/mol and $\Delta S_1^{\ddagger} = -2 \pm 1$ eu. For the aquation of $Ru(NH_3)_3N_2^{2+}$, $k_{-1} = 2.03 \times 10^{-6}\ sec^{-1}$ at 25.0°, $\Delta H_{-1}^{\ddagger} = 27.7 \pm 0.8$ kcal/mol, and $\Delta S_{-1}^{\ddagger} = 8 \pm 3$ eu.

Earlier experiments[1,2] showed $Ru(NH_3)_5N_2^{2+}$[3,4] and $[(Ru(NH_3)_5)_2N_2]^{4+}$ to be stable with respect to $Ru(NH_3)_5OH_2^{2+}$ and N_2 or $[Ru(NH_3)_5N_2]^{2+}$. Data on the rates of formation of the two complexes have been published,[5] and a recent communication[6] describes the results obtained in a calorimetric determination of $\Delta H°$ for the process

$$2Ru(NH_3)_5OH_2^{2+} + N_2(aq) = [(Ru(NH_3)_5)_2N_2]^{4+} + 2H_2O(liq)$$

It has also been reported[7] that over a period of 6 hr

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* To whom correspondence should be addressed.

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little, if any, exchange resulted between the coordinated nitrogen of $Ru(NH_3)_5N_2^{2+}$ and free nitrogen over the solution. All of the results mentioned have a bearing on the equilibrium constants for reactions 1 and 2, but

$$Ru(NH_3)_5OH_2^{2+} + N_2(aq) = Ru(NH_3)_5N_2^{2+} + H_2O\,(liq) \quad (1)$$

$$Ru(NH_3)_5OH_2^{2+} + Ru(NH_3)_5N_2^{2+} = [Ru(NH_3)_5N_2Ru(NH_3)_5]^{4+} + H_2O(liq) \quad (2)$$

the quantitative data on the important properties of the two systems are lacking. We report here the results of our determinations of the equilibrium constants for reactions 1 and 2 (K_1 and K_2), respectively, as a function of the temperature.

Experimental Section

Distilled water, redistilled from alkaline permanganate, was used in all experiments. Ionic strength was maintained by using NaCl–HCl mixtures.

$[Ru(NH_3)_5N_2]Br_2$ was prepared by reducing N_2O with Cr^{2+} in the presence of $[Ru(NH_3)_5OH_2]^{2+}$. $Ru(NH_3)_5Cl_3$ (0.6 g) was added to 330 ml of 0.1 *M* HCl. The solution was degassed with nitrous oxide prescrubbed through two wash solutions containing Cr^{2+}. An excess of Cr^{2+} (66 ml of 0.1 *M* solution) in a Cl^- medium was added to the vigorously stirred Ru(III) solution. After allowing the reaction to proceed for 1 hr, oxygen was passed through the solution to oxidize unreacted Cr^{2+} and $Ru(NH_3)_5OH_2^{2+}$. Solid NaBr was added until a cream-colored solid formed in the dark green solution. After cooling, the solid was removed by filtration and washed with methanol and acetone: yield 85% based on Ru used. The purity of the sample was confirmed by the uv absorbance (at 221 nm, ϵ 1.8×10^4; at 262 nm, ϵ 9×10^2), and by its infrared spectrum ($\nu_{N\equiv N}$ at 2110 cm^{-1} in KBr;[8] ν_{Ru-N_2} at 507 cm^{-1} in Nujol, 498 cm^{-1} in CsI.)[8] *Anal.* Calcd for $[Ru(NH_3)_5N_2]Br_2$: N, 26.2; Br, 42.7; H, 4.04; Ru, 27.0. Found: N, 26.4; Br, 42.9; H, 3.95; Ru, 27.8.

The equilibrium constant was determined by a static method in which $[Ru(NH_3)_5N_2]^{2+}$ was allowed to reach equilibrium at fixed N_2 activity, the concentrations of the aquo complex and the two nitrogen complexes then being determined, and by a dynamic method in which the rates of reactions 1 and 2, forward and reverse, were determined.

The analyses for $[Ru(NH_3)_5N_2]^{2+}$ and $[(Ru(NH_3)_5)_2N_2]^{4+}$ called for in using the static method for determining the equilibrium constants were performed by diluting a 1.00-ml aliquot of the equilibrated solution into 50.0 ml of air-saturated water and recording the absorbance at 262 and 221 immediately. The contribution of $[Ru(NH_3)_5N_2]^{2+}$ to the absorptivity at 262 nm is $\sim 9.0 \times 10^2$ M^{-1} cm^{-1}, and that of $[(Ru(NH_3)_5)_2N_2]^{4+}$ to the absorptivity at 221 nm is $\sim 3.0 \times 10^3$ M^{-1} cm^{-1}; these were allowed for in the final calculations. The concentration of $[Ru(NH_3)_5OH_2]^{2+}$ was determined by adding a 2.00-ml sample of the equilibrating solution to 1.00 ml of a deoxygenated solution 0.2 *M* in isonicotinamide contained in a 1-cm spectrophotometric cell. The absorption at 478 nm (ϵ 1.05×10^4 M^{-1} cm^{-1} for $[Ru(NH_3)_5isoamide]^{2+}$)[9] was recorded as a function of time using a Cary 15 spectrophotometer. There is a rapid initial reaction ($k \sim 0.06$ M^{-1} sec^{-1})[9] corresponding to the formation of the isoamide complex. This is followed by a much slower change ($k \sim 10^{-6}$ sec^{-1}) corresponding to further aquation of the complex. Correction for the second reaction was made by extrapolating the absorbance back to time zero.

Samples for the determination of the equilibrium constant by the static method were prepared by adding solid $[Ru(NH_3)_5N_2]Br_2$ to the reaction medium saturated with N_2 at atmospheric pressure. The solution was purged with N_2 for an additional 20 min and was then transferred to a series of 25-ml round-bottomed reaction flasks which had been flushed with N_2. Each flask was fitted with a 14/20 joint topped by a stopcock, the protruding end of the stopcock being closed by a serum cap. The ruthenium-containing solution was injected through the serum cap and the bore of the stopcock, and the needle was withdrawn while the flow of N_2 was maintained. The stopcock was closed, the serum cap was removed, and the stem was filled with wax. Wax was also used to secure the stopcock and joint seals. The flasks were covered with black tape and were stored in constant-temperature baths (±0.1°).

Because our ionic medium differed from that adopted by Itzkovitch and Page, we found it necessary, in using the dynamic method to determine the equilibrium constants, to repeat their measurements of the forward rates for reactions 1 and 2. Using low ruthenium concentrations, initial rates as measured by the absorbance at 221 nm yield accurate and reproducible values of k_1, with no significant interference by reaction 2. The rate of formation of $[(Ru(NH_3)_5)_2N_2]^{4+}$ was measured by the method of Itzkovitch and Page, using the reactants $[Ru(NH_3)_5N_2]^{2+}$ and $[Ru(NH_3)_5OH_2]^{2+}$ at equal concentrations.

The reverse rate for reaction 1 was determined by two methods. In one, a solution of $Ru(NH_3)_5N_2^{2+}$, prepared either by dissolving the bromide salt or by generating the ion by the action of excess Cr^{2+} on N_2O in the presence of the aquo ion, was saturated with Ar. The flasks, protected from light and maintained at 25°, were swept with Ar, and at intervals analyses for $[Ru(NH_3)_5N_2]^{2+}$, $[(Ru(NH_3)_5)_2N_2]^{4+}$, and $[Ru(NH_3)_5OH_2]^{2+}$ were made as already described. The concentration of $Ru(NH_3)_5OH_2^{2+}$ lost in the formation of $[(Ru(NH_3)_5)_2N_2]^{4+}$ (<12% after 24 hr) was taken into account in the calculation for the total $Ru(NH_3)_5OH_2^{2+}$ produced. The Ar used for degassing was passed through a solution containing Cr^{2+} and then through a solution of 0.1 *M* NaCl before it entered the reaction solution.

The alternative method depends upon using isonicotinamide to scavenge $Ru(NH_3)_5OH_2^{2+}$ as it is formed by aquation. In this method a solution of isonicotinamide was degassed with Ar inside a Zwickel flask.[10] Solid $[Ru(NH_3)_5N_2]Br_2$ was then added quickly by means of a side arm. The solution was degassed for an additional 20 min and then was pushed over into a 1-cm cell using an all-glass adaptor. The adaptor joints were sealed with wax and the cell was placed inside a thermostated Cary 15 compartment. The increase in absorbance at 478 nm resulting from the formation of $[Ru(NH_3)_5isoamide]^{2+}$ was followed as a function of time for approximately 24 hr.

Similar techniques were used in measuring the rate of aquation of the binuclear complex $[(Ru(NH_3)_5)_2N_2]^{4+}$.

The concentration of N_2 corresponding to a particular pressure was estimated using the value of the solubility given by Itzkovitch and Page at 25.0°. Other values were obtained by interpolation or extrapolation. The values[11] of C_{N_2}/P_{N_2} (M atm^{-1}) used in the calculation of the equilibrium constants are: 20.0°, 6.7×10^{-4}; 25.0°, 6.2×10^{-4}; 30.0°, 5.7×10^{-4}; 35.0°, 5.3×10^{-4}; 45.0°, 4.7×10^{-4}.

Where this was profitable the data providing the basis for the values of K_1 and K_2 were refined using a least-squares program[12] with a confidence limit of 50%.

Results

The results of the measurements of K_1 and K_2 by the static method are summarized in Table I. Approach to equilibrium is slow, and a complication in the method of determining $Ru(NH_3)_5OH_2^{2+}$ develops after a long period of time, manifested as a sharp drop in the apparent values of K_1 and K_2. We ascribe the difficulty to the release of NH_3 from the ammine complex. To the extent that this takes place, the concentration of $Ru(NH_3)_5OH_2^{2+}$, as determined using isonicotinamide to develop the color of ruthenium(II), will be too high, and the values of K_1 and K_2 will be correspondingly low. Ford, Kuempel, and Taube[13] have shown that the release of NH_3 on $Ru(NH_3)_6^{2+}$ is assisted by acid. In harmony with this result and our diagnosis of the complication, the effect is least severe at the lowest value of $[H^+]$, 4×10^{-4} *M*.

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Table I. Summary of the Measurements of K_1 and K_2 by the Static Method[a]

Conditions [HCl]$_0$	Temp, °C	Time, days	$K_1{}^b \times 10^{-4}$	$K_2{}^b \times 10^{-3}$
4.1×10^{-3}	25	8	3.9	3.0
		16	3.4	2.6
		22	2.5	2.2
4.1×10^{-3}	25	7	4.6	2.1
		14	3.7	2.6
		21	3.8	2.8
4.1×10^{-2}	25	14	3.3	10.2
		21	2.2	8.2
		31	1.6	7.2
4.1×10^{-2}	25	7	3.8	7.3
		15	2.9	8.9
		22	2.1	8.0
4.1×10^{-3}	25	7	4.8	6.8
		14	3.4	8.5
		21	3.3	9.6
		28	2.5	7.7
4.1×10^{-3}	25	7	4.1	5.6
		14	3.5	7.8
		21	3.0	8.2
4.1×10^{-4}	25	5	4.6	4.0
		11*	3.6	5.8
		22*	3.2	6.7
4.1×10^{-4}	25	5*	3.2	7.3
		21*	3.4	7.7
		38	4.3	9.5
4.1×10^{-4}	30	3	4.3	5.6
		7*	2.4	5.6
		15*	2.4	5.2
4.1×10^{-4}	30	3	3.4	4.2
		7*	2.8	5.9
		12*	2.5	5.3
		16*	2.8	5.9
4.1×10^{-4}	30	2	3.8	2.7
		4	3.1	4.3
		10*	2.7	5.4
		21*	2.7	5.3
4.1×10^{-4}	35	2	2.4	3.1
		4*	2.0	3.8
		11*	2.0	3.6
		15*	2.2	3.9
		22*	2.1	3.9
4.1×10^{-4}	35	5*	2.2	4.7
		10*	1.9	4.4
4.1×10^{-4}	35	2	2.2	3.3
		11*	2.3	4.8
		15*	2.2	4.6
4.1×10^{-4}	45	20* hr	1.1	2.3
		70* hr	1.3	2.2
4.1×10^{-4}	45	14* hr	1.2	2.1
		38* hr	1.1	2.2
		62* hr	1.2	2.4
4.1×10^{-4}	45	15* hr	1.2	2.4
		29* hr	1.0	2.2

[a] $[Ru(NH_3)_5N_2{}^{2+}]_0 = 2.50 \times 10^{-3}$ *M*. In a small number of cases $\Sigma[Ru(II)]_{tot}$ differed by more than 5% from 2.50×10^{-3} *M*. The results for such experiments were not reported. $\mu = 0.10$ except the first two experiments at 25°, where $\mu = 0.023$. [b] The standard state for all species in solution is 1 *M* and for H_2O it is the liquid.

As can be seen by following the apparent values of K_1 and K_2 as a function of time of reaction, the system appears to be more tractable at higher temperatures. Here the values of K_1 and K_2 appear to reach rather well-defined limits. At all temperatures, certain values need to be rejected, some when the time is too short to ensure equilibration, others when the time is so long that the analytical complication referred to makes itself felt. On this basis, all the data at higher acidities have been rejected for the purposes of calculating the equilibrium constants. The values for experiments marked with the asterisk have been selected. They are summarized in Table VI, where also are entered the values of $\Delta H°$ and $\Delta S°$ calculated from the data.

The kinetic data on the rates of formation of $[Ru(NH_3)_5N_2]^{2+}$ (k_1) and $[(Ru(NH_3)_5)_2N_2]^{4+}$ (k_2) are summarized in Tables II and III, respectively. Our value for k_1 at 25.0° agrees well with that reported by Itzkovitch and Page (7.1×10^{-2} M^{-1} sec^{-1} at 26°). Our values of k_2 do differ from theirs, but in view of the charge type of the reaction and the difference in ionic strength, this is not surprising. The data on k_1 as a function of temperature lead to values of 18.3 ± 0.3 kcal/mol and -2 ± 1 eu for $\Delta H_1{}^{\ddagger}$ and $\Delta S_1{}^{\ddagger}$, respectively.

Table II. Kinetic Data for the Formation of $Ru(NH_3)_5N_2{}^{2+}$[a]

Temp, °C	[HCl] × 10^3 *M*	μ	k_1, M^{-1} sec^{-1},[b,c] × 10^2
20.0	4.53	0.10	4.30
20.0	4.53	0.10	4.29
20.0	4.53	0.10	4.30
20.0	4.53	0.10	4.24
25.0	0.433	0.02	7.36
25.0	0.416	0.02	7.31
25.0	0.412	0.10	7.50
25.0	0.416	0.10	7.31
25.0	0.433	0.10	7.15
25.0	4.33	0.10	7.32
25.0	4.28	0.10	7.50
35.0	0.453	0.10	20.9
35.0	0.453	0.10	20.7
35.0	0.453	0.10	20.9
35.0	0.453	0.10	20.3

[a] $[Ru(NH_3)_5N_2{}^{2+}]_0 = 1.45 \times 10^{-3}$ *M*. [b] $N_2(aq)$ as the standard state. [c] The values listed in this column indicate the error associated with the value of k_1. In addition, there may also be a specific error in the values due to the error in the value for the solubility of nitrogen.

Table III. Formation of the Binuclear Complex from $Ru(NH_3)_5N_2{}^{2+}$ and $Ru(NH_3)_5OH_2{}^{2+}$[a]

[HCl] × 10^3 *M*	μ	$k_2 \times 10^2$ M^{-1} sec^{-1}
4.42	0.02	0.52
4.43	0.02	0.52
4.46	0.10	1.2
4.42	0.10	1.2
41.2	0.10	1.3
44.2	0.10	1.3

[a] $[Ru(NH_3)_5OH_2{}^{2+}]_0 \sim [(Ru(NH_3)_5)_2N_2{}^{4+}]_0 \sim 9.7 \times 10^{-4}$ *M*; temperature = 25.0°.

The data on the measurement of the rate of aquation of $[Ru(NH_3)_5N_2]^{2+}$, using a stream of Ar to remove N_2, are shown in Table IV. The method as we used it is

Table IV. The Rate of Aquation of $Ru(NH_3)_5N_2{}^{2+}$ as Measured by Removing N_2[a]

Time, hr	5.75	11	23	11	24	9.5	24
$k_{-1} \times 10^6$ sec^{-1} [b]	1.2	1.3	1.3	1.3	1.4	1.6	1.7

[a] $[Ru(NH_3)_5N_2{}^{2+}]_0 = 2.5 \times 10^{-3}$ *M*; temperature = 25.0°; $\mu = 0.10$; [HCl] = 4.1×10^{-2} *M*. [b] For the last experiment, $Ru(NH_3)_5N_2{}^{2+}$ was generated from N_2O and $Ru(NH_3)_5OH_2{}^{2+}$ using Cr^{2+}; for the remaining ones, $[Ru(NH_3)_5N_2]Br_2$ was used.

Table V. Measurement of the Rate of Aquation of $Ru(NH_3)_5N_2^{2+}$ Using Isonicotinamide to Remove $Ru(NH_3)_5OH_2^{2+}$

Temp, °C	$[Ru(NH_3)_5N_2^{2+}]_0 \times 10^4\ M$	$[\text{Isonicotinamide}]_0 \times 10^2\ M$	$[HCl] \times 10^3\ M$	μ[a]	$k_{-1} \times 10^6$, sec^{-1}
20.1	5.89	1.93	4.30	0.10	0.941
20.1	5.63	1.98	4.30	0.10	0.876
20.1	5.68	2.00	4.30	0.10	0.836
25.0	5.61	18.2	4.26	0.10	2.00
25.0	5.61	18.5	4.26	0.02	2.08
25.0	5.59	18.4	4.29	0.10	2.15
25.0	5.60	19.0	41.6	0.10	1.94
25.0	5.62	4.56	41.6	0.10	1.95
25.0	16.9	7.30	27.5	0.07	2.08
35.0	5.63	1.71	4.30	0.10	9.26
35.0	5.61	1.95	4.30	0.10	8.93
35.0	5.61	1.95	4.30	0.10	9.40
35.0	5.68	2.10	4.30	0.10	9.00

[a] Ionic strength maintained with NaCl-HCl.

neither precise nor accurate. Much better data were obtained using isonicotinamide to complex $[Ru(NH_3)_5OH_2]^{2+}$ as it is formed. The data obtained by measuring the rate of formation of $[Ru(NH_3)_5\text{isoamide}]^{2+}$ are summarized in Table V. The reaction was not followed over its entire course, data for the first 15% of reaction sufficing to define the rate. A spectrophotometric scan of the product complex showed precisely the characteristics expected for $[Ru(NH_3)_5\text{isoamide}]^{2+}$ (λ_{max} in the visible at 478 nm.)

The data in Table V show that the rate of formation of the isoamide complex is independent of the concentration of the ligand, as is expected of the rate-determining step in loss of N_2 from $[Ru(NH_3)_5N_2]^{2+}$. The agreement with the value of k_{-1} reported in Table IV also shows that isonicotinamide does not introduce a special complication into the measurements. The data on k_{-1} as a function of temperature lead to 27.7 ± 0.8 kcal/mol and 8 ± 3 eu for the kinetic parameters $\Delta H_{-1}^{\ddagger}$ and $\Delta S_{-1}^{\ddagger}$, respectively.

Attempts to measure the reverse rate of reaction 2 were not successful. The values of k_{-2} at 25.0° covered the range 2.7×10^{-6}–4.6×10^{-6} sec^{-1}. The rates appeared to depend on the age of the sample. For a fresh preparation, the rates were independent of the concentration of isonicotinamide in the range 0.09–0.19 M. However, with time a shoulder develops at ~400 nm on the main band. The rate at which absorption at 400 nm grows varies directly with the concentration of the ligand in the range 0.02–0.18 M.

Discussion

The equilibrium measurements are summarized in Table VI. Agreement between the static and kinetic methods is satisfactory, and we therefore believe that we have a true measure of the stability of $Ru(NH_3)_5N_2^{2+}$ with respect to $Ru(NH_3)_5OH_2^{2+}$ and N_2. The data for reaction 2 are not in such a satisfactory state, but in view of the constancy of the values of K_2, particularly at the higher temperatures, it is likely that they represent the equilibrium state within the limits of accuracy of the measurements. Because the equilibrium state of reaction 1 is not very sensitive to ionic strength, the data for this reaction will not be much altered by extrapolation to $\mu = 0$. The same is not true for reaction 2; a more exhaustive study will be needed to obtain for it values which can be extrapolated with confidence to the limit of $\mu = 0$.

Table VI. Summary of Data for K_1 and K_2[a]

Method of measurement	Temp, °C	$K_1 \times 10^{-4}$	$K_2 \times 10^{-3}$
Kinetic	20.1	4.9[b]	
Kinetic	25.0	3.6	
Static	25.0	3.3[c]	7.3[d,e]
Static	30.0	2.6	5.5
Kinetic	35.0	2.3	
Static	35.0	2.1	4.2
Static	45.0	1.2	2.3

[a] $\mu = 0.10$, chloride media. [b] $\Delta H_1° = -9.4 \pm 0.9$ kcal/mol; $\Delta S_1° = -10 \pm 3$ eu. [c] $\Delta H_1° = -10.1 \pm 1.4$ kcal/mol; $\Delta S_1° = -13 \pm 5$ eu at $[HCl] = 4.1 \times 10^{-4}\ M$. [d] $\Delta H_2° = -11.2 \pm 1.4$ kcal/mol; $\Delta S_2° = -20 \pm 5$ eu at $[HCl] = 4.1 \times 10^{-4}\ M$. [e] $K_2 \sim 2.5 \times 10^3$ at $\mu = 0.023$, $[HCl] = 4.1 \times 10^{-3}\ M$. $K_2 \sim 8.2 \times 10^3$ at $\mu = 0.10$, $[HCl] = 4.1 \times 10^{-3}\ M$.

The value of ΔH corresponding to the reaction of the aquo ion to form the binuclear complex, which we obtain by summing ΔH_1 and ΔH_2 as determined by the static method, is −21 ± 2 kcal/mol. This agrees satisfactorily with −22 ± 2 kcal/mol at $\mu = 0.4$ in an HSO_4^-–Cl^- medium obtained by direct measurement. The entropy change for reaction 1 is −13 ± 5 eu; this can be compared to the value −11 ± 4 eu measured for the formation of the N_2O complex.[14] It should be noted that a major part of the entropy change recorded is attributable to the fact that the standard states chosen for the solution and H_2O are different. If the hypothetical 1 M distribution were chosen as the standard state for H_2O, the value of K would increase, $\Delta F°$ would decrease, and $\Delta S°$ would increase to compensate for the change in $\Delta F°$. There may be other contributions as well, arising, for example, from an expected greater loss of rotational entropy for N_2O compared to H_2O when these species are transferred from the aqueous and liquid states, respectively, to the bound state, but these are probably minor.

The enthalpy of activation in the formation of $Ru(NH_3)_5N_2^{2+}$ is calculated as 18.3 ± 0.3 kcal/mol. This falls within the range of other values for substitution in $Ru(NH_3)_5OH_2^{2+}$ (17.6 ± 0.7 for N_2O, 17.5 ± 0.2 for pyrazine,[15] and 16.5 ± 0.8 kcal/mol for imidazole[15]). It seems likely, from a comparison of rates of substitution in this aquo ion, that the reaction takes place by a dissociative mechanism. If in fact an intermediate is

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(14) J. N. Armor and H. Taube, manuscript in preparation.

(15) R. Shepherd and H. Taube, submitted for publication.

formed, $\Delta H_{-1}^{\ddagger}$ (= 27.7 ± 0.8) then measures the strength of the bond between Ru(II) and N_2, while $\Delta H_1^{\ddagger}$ measures the strength of the bond between Ru(II) and H_2O.[16] A water molecule is undoubtedly a stronger base than N_2 when each forms only σ bonds. Thus, the extra stabilization which results from the involvement of the π orbitals of Ru is likely well in excess of 9 kcal/mol.[17]

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[16] A. E. Shilova and A. E. Shilov, *Kinet. Katal.*, **10**, 267 (1969). These authors conclude that the value of 23 kcal/mol which they measured as the activation energy for the decomposition of $RuN_2Cl_2(H_2O)_2 \cdot THF$ in THF corresponds to the energy of the Ru–N_2 bond.

[17] NOTE ADDED IN PROOF. C. Elson, I. J. Itzkovitch, and J. A. Page, *Can. J. Chem.*, **48**, 1639 (1970), recently reported a value of $\Delta H^{\ddagger}$ = 22.0 ± 0.1 kcal/mol for the formation of $Ru(NH_3)_5N_2^{2+}$. Part of the discrepancy in the results may lie in the values taken for the concentration of N_2 in solution. The values listed for the solubility of N_2 in water at various temperatures appear not to have been calculated by them with regard to the reference temperature listed in the table given in Stephen and Stephen.[11] For example, our values compare well with those obtained by other authors and techniques as listed in the "International Critical Tables" (Vol. 3, p 255): 25.0°, 6.32×10^{-4} *M;* 35.0°, 5.54×10^{-4} *M*. However, the difference in solubility does not completely explain all the differences in the results. Since we obtained similar results for ΔH_1° by both the static and kinetic methods and because of the similarity in the values of $\Delta H^{\ddagger}$ (16.5 to 19 kcal/mol) for the formation of $Ru(NH_3)_5X^{2+}$ complexes, where X is also N_2O (J. Armor and H. Taube, submitted for publication), and numerous neutral, nitrogen-base heterocycles (private communication with R. Shepherd and H. Taube), we believe that our value of $\Delta H_1^{\ddagger}$ is more nearly correct.

Determination of the Electronic Properties of Carboranes, Carborane Anions, and Metallocarboranes from Fluorine-19 Nuclear Magnetic Resonance Studies[1]

Robert G. Adler[2] and M. Frederick Hawthorne[3]

Contribution from the Department of Chemistry,
University of California, Riverside, California 92502.
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Abstract: The preparation of the carbon-substituted *m*- and *p*-fluorophenyl derivatives of a series of carboranes, carborane anions, and metallocarboranes allowed the electronic properties of these species to be determined from ^{19}F nmr chemical shifts and the method of Taft. Species examined in this manner include the 1,2 and 1,7 isomers of the $B_{10}C_2H_{12}$ icosahedral carboranes and the corresponding $B_9C_2H_{12}^-$ and $B_9C_2H_{11}^{2-}$ ions, as well as the 1,8-$B_9C_2H_{11}$ carborane and selected transition metal derivatives of the (3)-1,2- and (3)-1,7-$B_9C_2H_{11}^{2-}$ ions. In several instances large and negative $\sigma_R{}^0$ values were observed, which illustrates ground-state electron donation from the carborane moiety to the substituted phenyl ring by a π mechanism. The σ_I values were affected by both the relative carbon atom positions in the carborane fragments and the presence of a negative charge delocalized in those fragments.

Work reported in the past few years has served to reveal the extensive structural variations associated with the icosahedral $B_{10}C_2H_{12}$ carboranes and their derivatives. Of utmost interest is the similarity of 1,3- and 1,7-dicarbollide ions [(3)-1,2- and (3)-1,7-$B_9C_2H_{11}^{2-}$ ions][4] and their transition metal derivatives[5,6a] to the $C_5H_5^-$ ion and the common metallocenes derived from the $C_5H_5^-$ ion, respectively. The stereoelectronic properties associated with these and related structures have remained as unanswered questions although the electronic properties of the 1,2 and 1,7 icosahedral carboranes have been probed[6a] by a classical Hammett σ constant determination coupled with a Taft treatment of *m*- and *p*-fluorophenyl ^{19}F chemical shifts[6b,c] of suitable derivatives. The latter work[6a] revealed that the C-substituted 1,2 carboranyl group was similar in −I effect to the halogens and exhibited no ground-state resonance effect. Similar results have been reported by others using different experimental approaches.[7,8] On the other hand, the C-substituted 1,7-carboranyl group displayed a diminished −I effect and a very small ground-state resonance effect, electron releasing in nature.

It was obvious from the general agreement[6a] of the Taft method with the chemical equilibrium data that the former method could rather easily be employed to elucidate the electronic properties of an extended series of carborane structures. This paper reports the results of such a study which employed carborane carbon-bonded *m*- and *p*-fluorophenyl derivatives of the various carborane species investigated.

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[1] Taken in part from R. G. Adler, Ph.D. Dissertation, the University of California, Riverside, 1968.

[2] National Defense Education Act Fellow, 1964–1967; National Aeronautics and Space Administration Fellow, 1968.

[3] Address correspondence to this author at the University of California at Los Angeles, Los Angeles, California 90024.

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