Finally, sulfite ion would seem to be a fairly good nitrene trap for aqueous systems, but it has some serious drawbacks. It cannot be used in very acidic solution, and irradiation of any band at a wavelength lower than 260 nm cannot be carried out in its presence. However, the sulfamato complexes produced by the reaction of coordinated nitrene with sulfite ion are much more stable than the corresponding chloramine or hydroxylamine complexes prepared by this same type of reaction.[2] Also, the identification of the sulfamato complexes formed is assisted by the ability to prepare these compounds by other methods, and by the fingerprint characteristics of their ir spectra.

Acknowledgment. This research was supported by a grant from the National Science Foundation. The ruthenium and iridium used was loaned to us by the Matthey Bishop Co.

Registry No. $[Ir(NH_3)_5(NH_2SO_3)]Cl_2$, 51202-26-7; $[Ir(NH_3)_5(NHSO_3)]ClO_4$, 51202-28-9; $[Ru(NH_3)_5(N_3)]^{2+}$, 28223-30-5; $[Ru(NH_3)_5(NHSO_3)]^{+}$, 51259-39-3; $[Ir(NH_3)_5H_2O](ClO_4)_3$, 31285-82-2; $[Ir(NH_3)_5(N_3)](ClO_4)_2$, 38552-10-2; $[Ir(NH_3)_5NH_2OSO_3](ClO_4)_2$, 34412-12-9; SO_3^{2-}, 14265-45-3; $[Ru(NH_3)_5(NH_2SO_3)]^{2+}$, 51259-40-6.

Contribution from the Chemistry Department,
The University of Calgary, Calgary, Alberta, Canada T2N 1N4

Exchange of Oxygen-18 between Aquopentaammineiridium(III) Ion and Solvent Water. Pressure Effect and Mechanism

S. B. Tong and T. W. Swaddle*

Received December 17, 1973 AIC30895N

Borghi, Monacelli and Prosperi[1] have shown that the anation of $Ir(NH_3)_5OH_2^{3+}$ by chloride ion in acidic aqueous perchlorate solution proceeds by an interchange mechanism

$$Ir(NH_3)_5OH_2^{3+} + Cl^- \overset{K}{\rightleftharpoons} \{Ir(NH_3)_5OH_2^{3+}, Cl^-\} \xrightarrow{k_i} Ir(NH_3)_5Cl^{2+} + H_2O \qquad (1)$$

such that the rate of formation of the product is pseudo first order (rate coefficient k_{obsd}) in aquo complex at a given concentration of Cl^- in large excess, according to the relationship

$$k_{obsd} = \frac{k_iK[Cl^-]}{1 + K[Cl^-]} \qquad (2)$$

The rate coefficient k_i was significantly greater than that (k_{ex}) for the aquo exchange

$$Ir(NH_3)_5{}^{18}OH_2^{3+} + H_2O \xrightarrow{k_{ex}} Ir(NH_3)_5OH_2^{3+} + H_2{}^{18}O \qquad (3)$$

even when the influence of ion pairing on k_{ex} was considered, which suggests that $Ir(NH_3)_5OH_2^{3+}$ reacts by an associative interchange (I_a) mechanism.

The ion $Rh(NH_3)_5OH_2^{3+}$ behaves in a closely similar fashion,[2,3] and we have shown[4] that the measured volume of activation ΔV^* for aquo exchange in $Rh(NH_3)_5OH_2^{3+}$ confirms an associative mode of activation for simple aquo substitution in this complex.

Table I. First-Order Rate Coefficients k_{ex} for the Exchange of $H_2{}^{18}O$ between $Ir(NH_3)_5{}^{18}OH_2^{3+}$ and Solvent Water at 70.5° in 0.010 *M* $HClO_4$[a]

Pressure, kbars	10^5k, sec^{-1}	Pressure, kbars	10^5k, sec^{-1}
0.001	3.82 ± 0.08,[b] 3.96[b,c]	2.02	4.95 ± 0.23
0.059	4.01 ± 0.22	3.31	5.79 ± 0.41, 5.76 ± 0.21
1.027	4.56 ± 0.10	4.00	6.00 ± 0.29

[a] $[Ir(III)] = 0.041$ mol kg^{-1}. [b] In ordinary glass vessels. [c] Interpolated from data of ref 6.

Table II. Activation Parameters for Aquo Exchange of $M(NH_3)_5OH_2^{3+}$ in 0.01–0.10 *M* $HClO_4$

M	ΔV^*, cm^3 mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}	ΔH^*, kcal mol^{-1}
Co[a]	+1.2 ± 0.2	+6.7 ± 1.0	26.6 ± 0.3
Rh[b]	−4.1 ± 0.4	+0.8 ± 1.1	24.6 ± 0.3
Ir	−3.2 ± 0.1[c]	+2.7 ± 1.0[d]	28.1 ± 0.3[d]
Cr[b]	−5.8 ± 0.1	0.0 ± 1.6	26.2 ± 0.3

[a] H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, **80**, 2642 (1958). [b] Reference 4. [c] This work. [d] Recalculated from data of ref 6.

The primary objective of the present work was to seek support for the I_a mechanism, assigned by Monacelli, *et al.*,[1] to reaction 1, by evaluation of ΔV^* for reaction 3.

Experimental Section

Materials. $[Ir(NH_3)_5Cl]Cl_2$ was prepared from $K_3IrCl_6 \cdot 3H_2O$ (Alfa Inorganics) by the method of Basolo,[5] and the recrystallized product was converted to $[Ir(NH_3)_5OH_2](ClO_4)_3$ as described by Borghi and Monacelli.[6] The spectrum of the recrystallized product (maximum absorption at 258 nm, ϵ 85 M^{-1} cm^{-1}, and a shoulder at 333 nm, ϵ 12) agreed with that reported in the literature.[7] *Anal.* Calcd for $[Ir(NH_3)_5OH_2](ClO_4)_3$: N, 11.80. Found: N, 11.78. $[Ir(NH_3)_5OH_2](ClO_4)_3$ was recovered from the $[Ir(NH_3)_5Br]Br_2$ residues by the same procedure.

The oxygen-18-labeled aquo complex was prepared by maintaining a solution of the perchlorate salt in the minimum of water (1.7% $H_2{}^{18}O$, Bio-Rad Laboratories) at 94° for 24 hr, filtering, concentrating the filtrate, and allowing the product to crystallize at 0°.

Perchloric acid (71%, Baker Analyzed) was used without further purification. Distilled water was passed through Barnstead deionizer and organic removal cartridges before use.

Kinetics. A weighed amount of $[Ir(NH_3)_5OH_2](ClO_4)_3$ was dissolved in 30 g of 0.010 *M* $HClO_4$, quickly brought to the thermostat temperature, and placed in a preheated glass syringe which was promptly connected into the thermostated pressure assembly (±0.02°) described previously;[8] a Hastelloy B capillary outlet tube was used in these experiments, it having been established that aqueous iridium(III) ammines (unlike Co(III)[9]) do not react with this alloy. About 40–60 min was allowed after pressurization to ensure full thermal equilibration. Pressures were constant to within ±5 bars in the course of a run, except during sample withdrawal. Samples (3.0 ml, plus 1.0-ml "hold-up" which was rejected) were treated at once with 48% HBr (3.0 ml) at 0°, and the filtered $[Ir(NH_3)_5OH_2]Br_3$ was washed with acetone, dried *in vacuo*, and deaquated at temperatures *not exceeding 200°* on the vacuum line (higher temperatures led to general decomposition, evidently with evolution of N_2O). The liberated water was converted to CO_2 as described previously[4] and the ${}^{12}C^{16}O^{18}O$ content was determined relative to ${}^{13}C^{16}O_2$ (mean of 6–15 determinations, corrected for background; standard error *ca.* ±0.1%) using either a modified Nier isotope ratio spectrometer[10] or a Varian/MAT CH-5 mass spectrometer.

---

(1) E. Borghi, F. Monacelli, and T. Prosperi, *Inorg. Nucl. Chem. Lett.*, 6, 667 (1970).

(2) F. Monacelli, *Inorg. Chim. Acta*, 2, 263 (1968).

(3) H. L. Bott, A. J. Poe and K. Shaw, *J. Chem. Soc. A*, 1745 (1970).

(4) T. W. Swaddle and D. R. Stranks, *J. Amer. Chem. Soc.*, 94, 8357 (1972).

(5) F. Basolo, *Inorg. Chem.*, 1, 1 (1962).

(6) E. Borghi and F. Monacelli, *Inorg. Chim. Acta*, 5, 211 (1971).

(7) H. H. Schmidtke, *Inorg. Chem.*, 5, 1682 (1966).

(8) L. R. Carey, W. E. Jones, and T. W. Swaddle, *Inorg. Chem.*, 10, 1566 (1971).

(9) W. E. Jones, L. R. Carey, and T. W. Swaddle, *Can. J. Chem.*, 50, 2739 (1972).

(10) A. O. Nier, W. R. Eckelmann, and R. A. Lupton, *Anal. Chem.*, 34, 1358 (1962).

Table III. Spectroscopic Data, Ligand Field Splitting Parameters *Dq*,[a] Racah Parameters *B*′ and *C*′,[a] and Calculated Ligand Field Contributions LFAE to ΔH^* for the Aquo-Exchange Reactions,[b] for $M(NH_3)_5OH_2^{3+}$

	$Co(NH_3)_5OH_2^{3+}$	$Rh(NH_3)_5OH_2^{3+}$	$Ir(NH_3)_5OH_2^{3+}$
$^1T_{1g} \leftarrow {}^1A_{1g}$, cm^{-1}	20,600[c]	31,600[c]	38,800[d]
$^1T_{2g} \leftarrow {}^1A_{1g}$, cm^{-1}	29,400[c]	38,100[c]	47,000[d]
$^3T_{2g} \leftarrow {}^1A_{1g}$, cm^{-1}			30,000[d]
Dq, cm^{-1}	2500	3485	4320
B', cm^{-1}	550	406	513
C', cm^{-1}	4400[e]	3250[e]	4400
LFAE(C_{4v}) = $4Dq$, kcal mol^{-1}	29	40	49
LFAE(D_{3h}) = $11.52Dq - 3C'$, kcal mol^{-1}	45	87	105
LFAE(C_{2v}) = $8.86Dq$, kcal mol^{-1}	63	88	109
LFAE(D_{5h}) = $8.48Dq - 3C'$, kcal mol^{-1}	23	57	67

[a] Calculated using eq 9.11 of A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, New York, N. Y., 1968, assuming an O_h ligand field. [b] Calculated as by S. T. Spees, J. R. Perumareddi, and A. W. Adamson, *J. Amer. Chem. Soc.*, 90, 6626 (1968). [c] C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley, Reading, Mass., 1962. [d] A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, New York, N. Y., 1968, p 303. [e] Assuming $C' \approx 8B'$, since $C' = 7.5B'$ in $Co(NH_3)_6^{3+}$ [a,c] and $8.6B'$ in $Ir(NH_3)_5OH_2^{3+}$;[a,d] see also A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, New York, N. Y., 1968, p 307.

Results

The pseudo-first-order rate coefficients k_{ex} for aquo exchange, calculated as previously described,[4] are listed with their standard errors in Table I.

A plot of ln k_{ex} *vs.* pressure is linear, within the experimental error, and yields $\Delta V^* = -3.2 \pm 0.1$ cm^3 mol^{-1} with $k_{ex} = (3.96 \pm 0.05) \times 10^{-5}$ sec^{-1} at zero pressure and 70.5°. The latter value agrees satisfactorily with those determined directly at atmospheric pressure (Table I).

Discussion

Because solvent-exchange reactions are symmetrical and involve no change of charge, the interpretation of their ΔV^* values is relatively straightforward.[4] The only simple interpretation of $\Delta V^* = -3.2$ cm^3 mol^{-1} for the $Ir(NH_3)_5OH_2^{3+}$ aquo-exchange reaction is that the mechanism of simple aquo substitutions in this cation is associative (I_a), in confirmation of the conclusion reached by Borghi, *et al.*,[1] on quite different grounds.

The absolute value of ΔV^* also lends support to our previous contention[4] that ΔV^* for an associative aquo-exchange process should be numerically larger for complexes having voluminous, highly structured hydration sheaths than for those having less well-developed solvent shells. The ionic radii of the central M^{3+} ions in $M(NH_3)_5OH_2^{3+}$ are[11] 0.62 Å for Cr, 0.67 Å for Rh, and 0.73 Å for Ir, so that the centripetal electrostatic field acting to polarize the ligands of the first coordination sphere declines in the order Cr > Rh > Ir. The partial positive charges borne by the peripheral protons and consequently the extent of the solvation sheaths will therefore decrease in the same order. This is reflected in the decreasing magnitudes of $|\Delta V^*|$ for M = Cr, Rh, and Ir in Table II.

The striking anomaly of $Co(NH_3)_5OH_2^{3+}$ in Table II is attributable to the operation of an I_d mechanism[9,12,13] in this case, alone among those listed.[4] Indeed, since associative mechanisms seem to prevail in substitution reactions of $V(H_2O)_6^{3+}$,[14] $Mo(H_2O)_6^{3+}$,[15] and Ru(III) ammines,[16] as well as in the cases mentioned above, it may be that, *of the trivalent transition metal ions, only cobalt(III) forms cationic complexes which react by I_d mechanisms in simple substitution reactions.* Thus, the much studied cobalt(III) complexes, so far from providing models for octahedral substitution generally, may represent the exceptions rather than the rule for oxidation states III and above in cations.

A simple explanation for this anomalous behavior of cobalt(III) may lie in its very small ionic radius (0.53 Å, the smallest of all the trivalent transition metal ions encountered in typical octahedral complexes),[11] which results in severe steric strain even in the ground state of as simple an ion as $Co(NH_2CH_3)_5Cl^{2+}$.[17] Steric compression will therefore facilitate I_d and render I_a processes energetically inaccessible in most, if not all, Co(III) complexes; indeed, the effects on aquation rates of varying R in $M(NH_2R)_5Cl^{2+}$ support an I_a mechanism for M = Cr(III) and an I_d for M = Co(III).[18]

Ligand field effects might conceivably favor dissociative over associative mechanisms or *vice versa*. However, Table III summarizes some calculations after the manner of Spees, *et al.*,[19] of ligand field contributions (LFAE) to ΔH^* for likely I_d transition states of local symmetries C_{4v} and D_{3h} and I_a transition states of C_{2v} and D_{5h} geometries; it can be seen that the LFAE's for the $Rh(NH_3)_5OH_2^{3+}$ and $Ir(NH_3)_5OH_2^{3+}$ aquo exchanges far exceed the observed ΔH^* values (Table II), while one would erroneously predict an $I_a(D_{5h})$ mechanism for Co(III) and $I_d(C_{4v})$ for Rh and Ir, on this basis. Thus, the influence of ligand field effects on substitution reaction kinetics is evidently much less than commonly supposed and may require major theoretical reassessment.

Acknowledgments. We thank the National Research Council of Canada for financial support and Dr. H. R. Krouse and his staff for assistance with the mass spectrometry.

Registry No. $[Ir(NH_3)_5OH_2](ClO_4)_3$, 31285-82-2; H_2O, 7732-18-5.

---

(11) J. P. Jesson and E. L. Muetterties, "Chemist's Guide," Marcel Dekker, New York, N. Y., 1969.

(12) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, pp. 55-67.

(13) H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, 80, 2642 (1958).

(14) R. C. Patel and H. Diebler, *Ber. Bunsenges. Phys. Chem.*, 76, 1035 (1972).

(15) Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 767 (1973).

(16) J. A. Broomhead and L. A. P. Kane-Maguire, *Inorg. Chem.*, 7, 2519 (1968).

(17) B. M. Foxman, *J. Chem. Soc., Chem. Commun.*, 515 (1972).

(18) G. Guastalla and T. W. Swaddle, *Can. J. Chem.*, 51, 821 (1973).

(19) S. T. Spees, J. R. Perumareddi, and A. W. Adamson, *J. Amer. Chem. Soc.*, 90, 6626 (1968).