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# Calculated Volume and Energy Profiles for Water Exchange on $t_{2g}^6$ Rhodium(III) and Iridium(III) Hexaaquaions: Conclusive Evidence for an $I_a$ Mechanism

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An $I_a$ mechanism was assigned for water exchange on the hexaaquaions $Rh(OH_2)_6^{3+}$ and $Ir(OH_2)_6^{3+}$ on the basis of negative $\Delta V^‡$ experimental values (–4.2 and –5.7 cm$^3$ mol$^{-1}$, respectively). The use of $\Delta V^‡$ as a mechanistic criterion was open to debate primarily because $\Delta V^‡$ could be affected by extension or compression of the nonparticipating ligand bond lengths on going to the transition state of an exchange process. In this paper, volume and energy profiles for two distinct water exchange mechanisms (D and $I_a$) have been computed using quantum chemical calculations which include hydration effects. The activation energy for $Ir(OH_2)_6^{3+}$ is 32.2 kJ mol$^{-1}$ in favor of the $I_a$ mechanism (127.9 kJ mol$^{-1}$), as opposed to a D pathway; the value for the $I_a$ mechanism being close to $\Delta H^‡$ and $\Delta G^‡$ experimental values (130.5 kJ mol$^{-1}$ and 129.9 kJ mol$^{-1}$ at 298 K, respectively). Volumes of activation, computed using Connolly surfaces and for the $I_a$ pathway ($\Delta V^‡_{calc} = –3.9$ and –3.5 cm$^3$ mol$^{-1}$, respectively, for $Rh^{3+}$ and $Ir^{3+}$), are in agreement with the experimental values. Further, it is demonstrated for both mechanisms that the contribution to the volume of activation due to the changes in bond lengths between Ir(III) and the spectator water molecules is negligible: –1.8 for the D, and –0.9 cm$^3$ mol$^{-1}$ for $I_a$ mechanism. This finding clarifies the debate about the interpretation of $\Delta V^‡$ and unequivocally confirms the occurrence of an $I_a$ mechanism with retention of configuration and a small a character for both Rh(III) and Ir(III) hexaaquaions.

## Introduction

Ever since the pioneering work of Eigen and Wilkins[1] which showed that, for aqueous solutions, the rates and activation parameters for ligand substitution were closely similar to those of solvent exchange, the study of the latter process has assumed fundamental importance. Accordingly, interest in the water exchange process has blossomed over the years resulting in one of the largest compilations of information about ligand substitution to date, encompassing 20 orders of magnitude variation of the water exchange rate constant (Figure 1).

Water exchange reactions on di- and trivalent transition metal aquaions have been the subject of extensive experimental studies and have been widely reviewed.[2,3] For 3d octahedral metal ions, the water exchange mechanism progressively changes from $I_a$ to $I_d$ as the number of d-electrons increases and the ionic radius decreases. This change is demonstrated most evidently by the change in the sign of the activation volume $\Delta V^‡$ and has been confirmed by Rotzinger[4,5] who performed calculations at the Hartree–Fock and CAS-SCF levels. It has been observed that the progressive mechanistic changeover cannot be explained in terms of cationic size only, the electronic configuration also playing an important role. For a σ-bonded octahedral

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(1) (a) Eigen, M. *Z. Elektrochem.* **1960**, *64*, 115. (b) Eigen, M. *Pure Appl. Chem.* **1963**, *6*, 97. (c) Eigen, M.; Wilkins, R. G. *Adv. Chem. Ser.* **1965**, *49*, 55.

(2) Helm, L.; Merbach, A. E. *Coord. Chem. Rev.* **1999**, *187*, 151.

(3) Dunand, F. A.; Helm, L.; Merbach, A. E *Adv. Inorg. Chem.* **2003**, *54*, 1.

(4) Rotzinger, F. P. *J. Am. Chem. Soc.* **1996**, *118*, 6760.

(5) Rotzinger, F. P. *J. Am. Chem. Soc.* **1997**, *119*, 5230.

10.1021/ic035096n CCC: $27.50

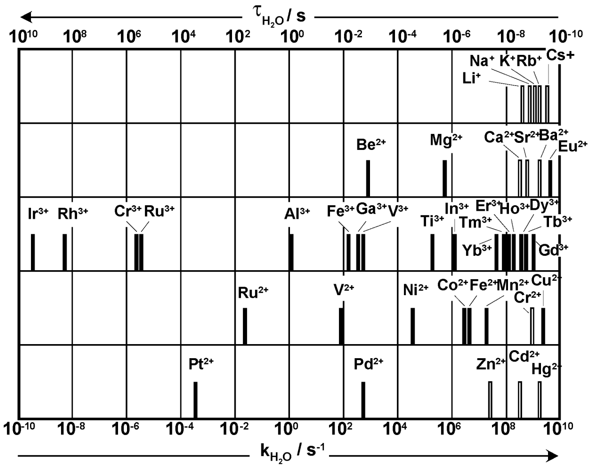

**Figure 1.** Mean lifetimes of a particular water molecule in the first coordination sphere of a given metal ion, $\tau_{H_2O}$, and the corresponding water exchange rate constants, $k_{H_2O}$, at 298 K. The filled bars indicate directly determined values, and the empty bars indicate values deduced from ligand substitution studies.

complex, the $t_{2g}$ orbitals are nonbonding, whereas the $e_g$* orbitals are antibonding. The gradual filling of the $t_{2g}$ orbitals, spread out between ligands, will electrostatically disfavor the approach of a seventh molecule toward a face or edge of the octahedron and therefore decrease the ease of bond-making. Similarly, an increased occupancy of the $e_g$* orbitals, pointed to the ligands, will increase the bond-breaking tendency. It was established that the electronic effects could therefore explain the changeover of mechanism, but the problem is not so simple.

According to these arguments, one would predict a dissociative activation mode for water exchange on the low spin $t_{2g}^6$ hexaaqua ions $Ru(OH_2)_6^{2+}$, $Rh(OH_2)_6^{3+}$, and $Ir(OH_2)_6^{3+}$. In a first study of the mechanism of substitution on $Ru(OH_2)_6^{2+}$, it was shown that the rate constants for the anation reactions by $Cl^-$, $Br^-$, and $I^-$ were very similar indicating identical steps to reach the transition state (i.e., dissociation of an $H_2O$ ligand).[6] Later, this study was extended to a large variety of ligands possessing various charges and nucleophilicities, and it was clearly demonstrated that the rate of the monocomplex formation reactions was independent of the nature of the entering ligand. An $I_d$ mechanism was therefore attributed for the substitution reactions on $Ru(OH_2)_6^{2+}$.[7] However, a variable pressure study of water exchange on this ion gave an activation volume close to zero ($\Delta V^‡ = -0.4$ cm$^3$ mol$^{-1}$) and was therefore interpreted as an interchange I mechanism without predominant a or d character.[8]

The $Rh(OH_2)_6^{3+}$ and $Ir(OH_2)_6^{3+}$ aquaions have been even more intriguing. In the 1970s, Harris and co-workers found virtually identical rate constants and similar activation enthalpies for substitution on $Rh(OH_2)_6^{3+}$ by $Cl^-$ and $Br^-$ ions and by $H_2O$ and concluded a dissociative D mechanism.[9] A few years ago, a negative volume of activation for water exchange on $Rh(OH_2)_6^{3+}$ ($-4.2$ cm$^3$ mol$^{-1}$)[10] and an even more negative one for $Ir(OH_2)_6^{3+}$ ($-5.7$ cm$^3$ mol$^{-1}$),[11] was obtained, and it was concluded in both cases to be an associative interchange $I_a$ mechanism. Recently, we performed a theoretical study of water exchange on $t_{2g}^6$ aquaions,[12] and we correlated the negative changes ($-0.534$ Å) of the sum of all Rh−O bond lengths, $\Delta\sum d$(Rh−O), during the activation process with the experimental volume of activation $\Delta V^‡$, and concluded an $I_a$ mechanism, too. In a recent experimental study of the $Br^-$ anation on the Rh(III) aquaion, Richens and co-workers[13] showed that the formation of the bromo complex $Rh(OH_2)_5Br^{2+}$ from the aquaion $Rh(OH_2)_6^{3+}$ follows an associatively activated concerted mechanism $I_a$, whereas the successive bromations follow dissociatively activated mechanisms $I_d$. These authors attribute the discrepancy in the assignment of water substitution mechanism on the Rh(III) aquaion to an erroneous interpretation of the kinetic data by Harris and co-workers.[9]

Nevertheless, the general question of whether a $t_{2g}^6$ system can undergo ligand substitution associatively, defying the molecular orbitals theory and the 18-electron rule, still requires further investigations, as suggested by Dhungana et al.[14] It is the goal of the present study to complete our previous research of water exchange on $Ru(OH_2)_6^{2+}$ and $Rh(OH_2)_6^{3+}$ with an extension to $Ir(OH_2)_6^{3+}$, and by simulating the activation volumes of these processes to clarify this debate.

## Computational Details

All calculations were performed on SGI workstations using the GAMESS[15] and the GAUSSIAN 98[16] programs. The basis sets of Stevens et al.[17] were used for iridium, where the 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, and 4f shells are represented by relativistic effective

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(6) Kallen, T. W.; Earley, J. E. *Inorg. Chem.* **1971**, *10*, 1149.

(7) Aebischer, N.; Laurenczy, G.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1993**, *32*, 2810.

(8) Rapaport, I.; Helm, L.; Merbach, A. E.; Bernhard, P.; Ludi, A. *Inorg. Chem.* **1988**, *27*, 873.

(9) (a) Plumb, W.; Harris, G. M. *Inorg. Chem.* **1964**, *3*, 542. (b) Buchacek, R. J.; Harris, G. M. *Inorg. Chem.* **1976**, *15*, 926. (c) Swaminathan, K.; Harris, G. M. *J. Am. Chem. Soc.* **1966**, *88*, 4411.

(10) Laurenczy, G.; Rapaport, I.; Zbinden, D.; Merbach, A. E. *Magn. Reson. Chem.* **1991**, *29*, S45.

(11) Cusanelli, A.; Frey, U.; Richens, D. T.; Merbach, A. E. *J. Am. Chem. Soc.* **1996**, *118*, 5265.

(12) De Vito, D.; Sidorenkova, H.; Rotzinger, F. P.; Weber, J.; Merbach, A. E. *Inorg. Chem.* **2000**, *39*, 5547.

(13) Galbraith, S. C.; Robson, C. R.; Richens, D. T. *J. Chem. Soc., Dalton Trans.* **2002**, 4335.

(14) Dhungana, S.; Crumbliss, A. L. *Chemtracts* **2001**, *14*, 42.

(15) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(17) Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612.

core potentials, the 5s, 5p, and 6s shells exhibit double-$\zeta$ quality, and the 5d shell has triple-$\zeta$ quality. For oxygen and hydrogen atoms, the 6-31G[18,19] basis set supplemented with a 3d polarization function ($\alpha_{3d}(O) = 1.20$)[20] was used.

All the calculations, in particular the location of the transition states, were performed with the method and approximations previously described by Rotzinger.[4,5] The ab initio calculations have been carried out at the restricted Hartree−Fock (SCF) level, studies of Rotzinger[4,5] and De Vito et al.[12] having shown that this level of theory leads to satisfactory results. This allowed us to characterize two water exchange mechanisms (dissociative and interchange) for the Ir(III) hexaaqua ion. Additional calculations performed using DFT methods (with the GAUSSIAN 98 program package) with different functionals (local and nonlocal) have been carried out, but no satisfactory results have been found for transition states or intermediates.

The geometries of reactants, transitions states, and pentacoordinated intermediate (for the D mechanism) were optimized at the Hartree−Fock level by taking into account solvation using the self-consistent reaction field model (SCRF)[21,22] implemented in the GAMESS program.[23] For the SCRF calculations, the cavity radius was taken as half of the value of the largest interatomic H−H distance plus the two corresponding van der Waals radii. Once the geometry had converged, the cavity radius was redetermined, and if it differed by more than 0.01 Å from the previous value, the geometry optimization was repeated until the above criterion was fulfilled. Energies of these species were then computed on the basis of PCM polarizable continuum model[24−28] using the GAMESS program.

The volumes of the aqua clusters were calculated from solvent excluding surfaces (Connolly surfaces[29]) by using the MOLEKEL package.[30] They were calculated with a probe radius of 1.40 Å and a dot density of 100 $Å^{-2}$, and by neglecting the volume of the hydrogen atoms.

## Results

**Model and Approximations.** The water exchange of the hexaaqua ion of iridium(III) (eq 1) was studied on the basis of the model previously described by Rotzinger.[4,5]

$$[\mathrm{Ir(OH_2)_6}]^{3+} + 6\mathrm{H_2{*}O} \rightleftharpoons [\mathrm{Ir({*}OH_2)_6}]^{3+} + 6\mathrm{H_2O} \qquad (1)$$

It involves the transition metal ion and 6 water molecules for the dissociative D mechanism (eq 2), and 7 water molecules for the associative A (eq 3) and the interchange I mechanisms (eq 4).

$$[\mathrm{Ir(OH_2)_6}]^{3+} \rightarrow \{[\mathrm{Ir(OH_2)_5}\cdots(\mathrm{OH_2})]^{3+}\}^{\ddagger} \qquad (2)$$

$$[\mathrm{Ir(OH_2)_6}\cdot(\mathrm{OH_2})]^{3+} \rightarrow \{[\mathrm{Ir(OH_2)_6}\cdots(\mathrm{OH_2})]^{3+}\}^{\ddagger} \qquad (3)$$

$$[\mathrm{Ir(OH_2)_6}\cdot(\mathrm{OH_2})]^{3+} \rightarrow \{[\mathrm{Ir(OH_2)_5}\cdots(\mathrm{OH_2})_2]^{3+}\}^{\ddagger} \qquad (4)$$

The geometries were optimized for all stationary points along the reaction paths: reactants/products, transition states, and intermediates (Figures 2 and 3) as previously described,[12] and the results are given in Table 1.

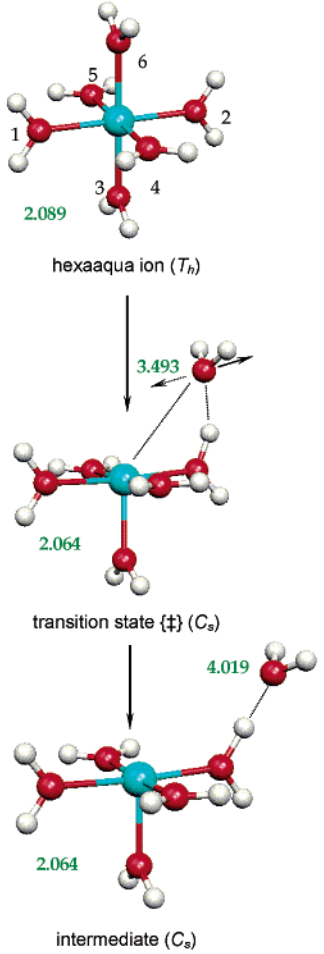

**Figure 2.** Reactant, transition state, and intermediate for the dissociative D mechanism. The Ir−O distances (average for the spectator ligands 1−5) are indicated on the left, and M−O(6) are on the right. The imaginary mode for the transition state is indicated by arrows.

The changes of the sum of all Ir−O bond lengths, $\Delta\sum d(\mathrm{Ir{-}O})$ (eq 5), during the activation process is related to the intrinsic component $\Delta V^{\ddagger}_{\mathrm{int}}$ of the activation volume. For the metal hexaaqua ions, the sign of $\Delta\sum d(\mathrm{M{-}O})$ was found to be the same as that of $\Delta V^{\ddagger}_{\mathrm{int}}$.[4,5]

$$\Delta\sum d(\mathrm{Ir{-}O}) = \sum d(\mathrm{Ir{-}O})_{\mathrm{transitionstate}} - \sum d(\mathrm{Ir{-}O})_{\mathrm{reactant}} \qquad (5)$$

Merbach et al.[31] have successfully computed activation volumes, $\Delta V^{\ddagger}_{\mathrm{calc}}$, on the basis of the Connolly surfaces.[29]

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(18) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(19) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(20) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(21) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351.

(22) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.

(23) Szafran, M.; Karelson, M. M.; Katritzky, A. R.; Koput, J.; Zerner, M. C. *J. Comput. Chem.* **1993**, *14*, 371.

(24) Miertus, S.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1981**, *55*, 117.

(25) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.

(26) Cammi, R.; Tomasi, J. *J. Comput. Chem.* **1995**, *16*, 1449.

(27) Barone, V.; Cossi, M.; Tomasi, J. *J. Comput. Chem.* **1998**, *19*, 407.

(28) Barone, V.; Cossi, M. *J. Phys. Chem. A.* **1998**, *102*, 1995.

(29) Connolly, M. L. *J. Appl. Crystallogr.* **1983**, *16*, 548.

(30) Flükiger, P. F. Development of the molecular graphics package MOLEKEL and its application to selected problems in organic and organometallic chemistry. Thèse No. 2561, Département de chimie physique, Université de Genève, Genève, 1992.

(31) Kowall, Th.; Caravan, P.; Bourgeois, H.; Helm, L.; Rotzinger, F. P.; Merbach, A. E. *J. Am. Chem. Soc.* **1998**, *120*, 6569.

**Table 1.** Geometric and Thermodynamic Parameters Calculated (HF Level) for the Ir(III) Species in Gas Phase and with Inclusion of Hydration Effects

| | symmetry | $\Delta E^{\ddagger}$, kJ mol$^{-1}$ gas phase | PCM[b] | $d$(Ir−O), Å calcd[c] | exptl | $\Delta\Sigma d$(Ir−O), Å | $\Delta V^{\ddagger}_{calc}$,[e] cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | | D Mechanism | | | |
| $[Ir(OH_2)_6]^{3+}$ | $T_h$[a] | | | 2.089; 2.089; 2.089; 2.089; 2.089; 2.089 | 2.041[d] | | |
| $\{[Ir(OH_2)_5\cdots(OH_2)]^{3+}\}^{\ddagger}$ | $C_s$ | 146.1 | 160.1 | 2.100; 2.042; 2.027; 2.074; 2.074; 3.493 | | +1.282 | +5.5 (+6.3)[f] |
| $[Ir(OH_2)_5\cdot(OH_2)]^{3+}$ | $C_s$ | 143.1 | 155.9 | 2.105; 2.039; 2.027; 2.074; 2.074; 4.019 | | +1.805 | +7.1 (+8.2)[f] |
| | | | | $I_a$ Mechanism | | | |
| $[Ir(OH_2)_6\cdot(OH_2)]^{3+}$ | $C_1$ | | | 2.104; 2.072; 2.092; 2.088; 2.088; 2.077; 3.832 | 2.041[d] | | |
| $\{[Ir(OH_2)_5\cdots(OH_2)_2]^{3+}\}^{\ddagger}$ | $C_2$ | 144.6 | 127.9 | 2.076; 2.076; 2.049; 2.085; 2.085; 2.741; 2.741 | | −0.501 | −3.5 (−3.9)[f] |

[a] Optimized in $D_{2h}$ symmetry. [b] Energies obtained using SCRF geometries. [c] Distances obtained using SCRF model. In the order of the oxygen numbering in Figures 2 and 3. [d] Average from X-ray structure of $Cs[Ir(OH_2)_6](SO_4)_2\cdot 6H_2O$, ref 42. [e] Values computed using the Connolly surface method. [f] In parentheses are given the values calculated for $Rh(OH_2)_6^{3+}$.

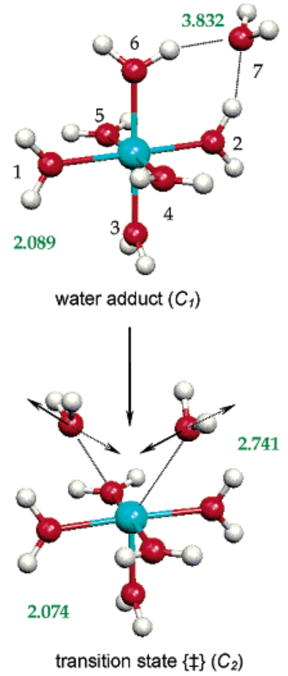

**Figure 3.** Reactant and transition state for the associative interchange $I_a$ mechanism. The Ir−O distances (average for the spectator ligands 1−5) are indicated on the left, and Ir−O(7) are on the right. The imaginary frequency mode for the transition state is indicated by arrows.

We used this method to calculate the volumes of reactants, transition states, and intermediate (if any), and in an empirical approach, we neglected the volume of the hydrogen atoms and scaled up the van der Waals radius of the water oxygen by a factor of 1.254 as previously done to reproduce the experimental $\Delta V^{\ddagger}$ for Al(III) and Ga(III).[31] The calculated values are given in Table 1, and to allow a comparison with the isoelectronic aquaion Rh(III), the $\Delta V^{\ddagger}_{calc}$ values for the two mechanisms previously calculated[12] for water exchange on $Rh(OH_2)_6^{3+}$ have also been computed.

As shown in Table 1, the Hartree−Fock method is adequate to describe the iridium(III) aquaion, as it can be seen from the comparison of calculated and experimental Ir−O bond lengths of $Ir(OH_2)_6^{3+}$. The differences are the same as that for other hexaaqua ions; the calculated Ir−O bond lengths are systematically slightly too long (0.048 Å) due to approximations already discussed.[4,5,32]

**Water Exchange Mechanisms.** Two transition states have been obtained from calculations: one for the dissociative D mechanism (Figure 2) and one for the interchange I mechanism (Figure 3). For the D mechanism, an intermediate with reduced coordination number and characterized by all real vibrational frequencies has been obtained, whereas no intermediate has been found for the I mechanism (this allows us to straightforwardly assign an I mechanism vs a limiting associative A one).

It has been shown for water exchange that geometries are generally quite insensitive to hydration effects,[33] but that hydration has to be taken into account for calculation of energies. Thus, applying the PCM hydration model, the activation energy for the water exchange on iridium(III) via the I mechanism was found to be clearly lower (by 32.2 kJ mol$^{-1}$) than that via the D pathway (Table 1, Figure 4), and the computed $\Delta E^{\ddagger}$ for the interchange mechanism agrees very well with $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ experimental values[11] (130.5 and 129.9 kJ mol$^{-1}$ at 298 K, respectively). For the I mechanism, the change of the sum of all Ir−O bond lengths, $\Delta\sum d$(Ir−O), to reach the transition state (−0.501 Å), and the computed volume of activation $\Delta V^{\ddagger}_{calc}$ (−3.5 cm$^3$ mol$^{-1}$) are both negative, as the experimental $\Delta V^{\ddagger}$ value.

## Discussion

The usual approach to elucidate the mechanism of substitution reactions involves the study of the dependence of the reaction rate on reactants concentration, pH, ionic strength, and solvent composition. For solvent exchange on metal ions, these criteria are not applicable. Therefore, one has to rely, beside theoretical simulation, on the activation parameters obtained from variable temperature and pressure studies.[34] In this context, the chief advantage of the volume of activation, $\Delta V^{\ddagger}$, is that it can be easily understood in terms of atomic movements alone; the interpretation of $\Delta S^{\ddagger}$, on the other hand, involves less tangible factors such as molecular energy levels (translational, rotational, vibrational) and the mode of occupation thereof, together with contributions from solvent ordering. Volume changes on the macroscopic scale are directly perceptible by the human senses, whereas entropy is a transcendent abstraction. Further,

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(32) Åkesson, R.; Petterson, L. G. M.; Sandström, M.; Wahlgren, U. *J. Am. Chem. Soc.* **1994**, *116*, 8691.

(33) Rotzinger, F. P. *J. Phys. Chem. A* **1999**, *103*, 9345.

(34) (a) Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479. (b) Merbach, A. E. *Pure Appl. Chem.* **1987**, *59*, 161.

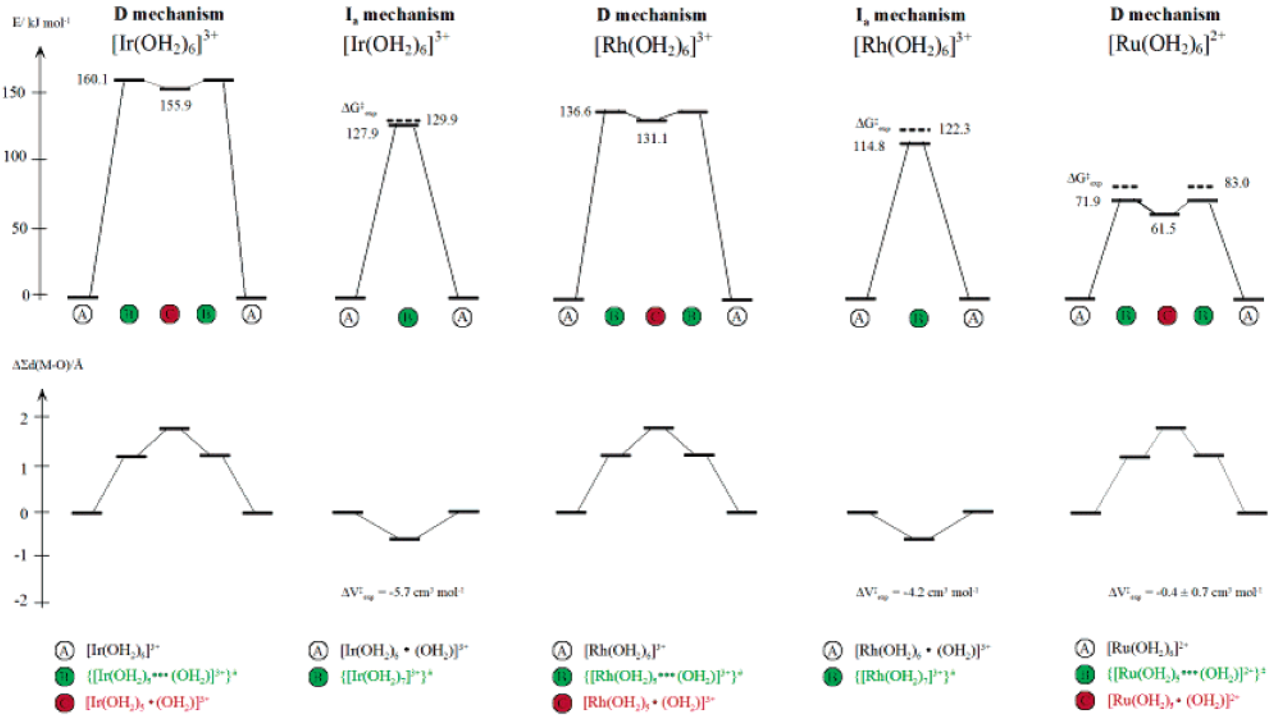

**Figure 4.** PCM energies, $\Delta\sum d$(M−O) in Å (eq 5), and energy profiles for water exchange on iridium(III), rhodium(III), and ruthenium(II) hexaaquaions.

because a long graphical extrapolation is needed to obtain $\Delta S^\ddagger$, their values are less accurate than $\Delta V^\ddagger$. Thus, one may theorize about $\Delta V^\ddagger$, as suggested by Swaddle,[35] with much more confidence than in the cases of $\Delta S^\ddagger$. It must also be remembered that for substitution reactions in general, the experimentally determined $\Delta V^\ddagger$ is usually discussed in terms of the sum of an intrinsic contribution, $\Delta V^\ddagger_{\text{int}}$, arising from changes in the internuclear distances during the formation of the transition state, and an electrostrictive contribution, $\Delta V^\ddagger_{\text{elec}}$.[36] Likely, there is no overall charge creation or annihilation during a solvent exchange reaction, and for an octahedral aquaion in water, the change in dipole moment by going to the transition state will not produce a significant change in electrostriction.[35,36] Therefore, the experimentally determined value gives directly the $\Delta V^\ddagger_{\text{int}}$, showing either a bond breaking or a bond making prevalence during the activation process.

Let us revisit some experimental evidence. The negative volume (−5.7 $\text{cm}^3\ \text{mol}^{-1}$) and near zero entropy (+2.1 $\text{cm}^3$ $\text{mol}^{-1}$) of activation obtained for $\text{Ir(OH}_2)_6^{3+}$ by Merbach et al.[11] is supportive of an associative activation mode a for the water exchange process on this aquaion. However, to differentiate between an associative interchange $\text{I}_a$ and a limiting associative A mechanism, the magnitude of $\Delta V^\ddagger$ has to be considered. The experimentally determined value is less negative than that calculated for first-row metal 3d ions for an A mechanism (±13.5 $\text{cm}^3\ \text{mol}^{-1}$ for limiting dissociative and associative mechanisms according to Swaddle's semiempirical model[37]) and, more importantly, significantly less negative than the most negative experimental value ($\text{Ti}^{3+}$, −12.1 $\text{cm}^3\ \text{mol}^{-1}$).[38] Thus, the water exchange mechanism on the hexaaqua iridium(III) seems to be best represented as an associative interchange mechanism $\text{I}_a$. A similar mechanism has been assigned to the trivalent metal hexaaqua ions $\text{Fe}^{3+}$, $\text{Cr}^{3+}$, $\text{Ru}^{3+}$, and $\text{Rh}^{3+}$.[2] In contrast, the mechanistic assignment for water exchange on the hexaaqua ions of $\text{Al}^{3+}$ (+5.7 $\text{cm}^3\ \text{mol}^{-1}$) and $\text{Ga}^{3+}$ (+5.0 $\text{cm}^3\ \text{mol}^{-1}$) was much less straightforward.[39] By comparison with the limiting value for the dissociative mechanism, an $\text{I}_d$ mechanism was assigned. However, more recent theoretical calculations have highlighted a D mechanism with an intermediate with reduced coordination number that gives energies and volumes fully compatible with experimental data.[31]

As already said, an associatively activated water exchange is a priori electronically disfavored on $\text{t}_{2g}^6$ aquaions. On the basis of experimental activation volumes, an I mechanism was assigned to $\text{Ru(OH}_2)_6^{2+}$ (−0.4 $\text{cm}^3\ \text{mol}^{-1}$),[8] and an $\text{I}_a$ mechanism to $\text{Rh(OH}_2)_6^{3+}$ (−4.2 $\text{cm}^3\ \text{mol}^{-1}$)[10] and $\text{Ir(OH}_2)_6^{3+}$ (−5.7 $\text{cm}^3\ \text{mol}^{-1}$).[11] In a previous theoretical study,[12] all attempts to compute a transition state for an interchange mechanism for Ru(II) failed, and a D mechanism, without excluding $\text{I}_d$, was assigned. In contrast, two pathways could be characterized for Rh(III) corresponding to D and $\text{I}_a$ mechanisms (Figure 4). It was shown that the greater charge of Rh(III) especially affects the M−O bond strengths. The $\text{Rh}^{\text{III}}$−O bonds are considerably stronger than the $\text{Ru}^{\text{II}}$−O bonds, disfavoring the D mechanism for the rhodium(III) aquaion. For Rh(III), the $\Delta G^\ddagger_{\text{exp}}$ lies between the activation energies computed for the D and I mechanism. Interestingly, for Ir(III) the difference in energies found in the present study

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(35) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.
(36) Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479.
(37) Swaddle, T. W. *Inorg. Chem.* **1983**, *22*, 2663.
(38) Hugi, A. D.; Helm, L.; Merbach, A. E. *Inorg. Chem.* **1987**, *26*, 1763.
(39) Hugi-Clearly, D.; Helm, L.; Merbach, A. E. *Helv. Chim. Acta* **1985**, *68*, 545.

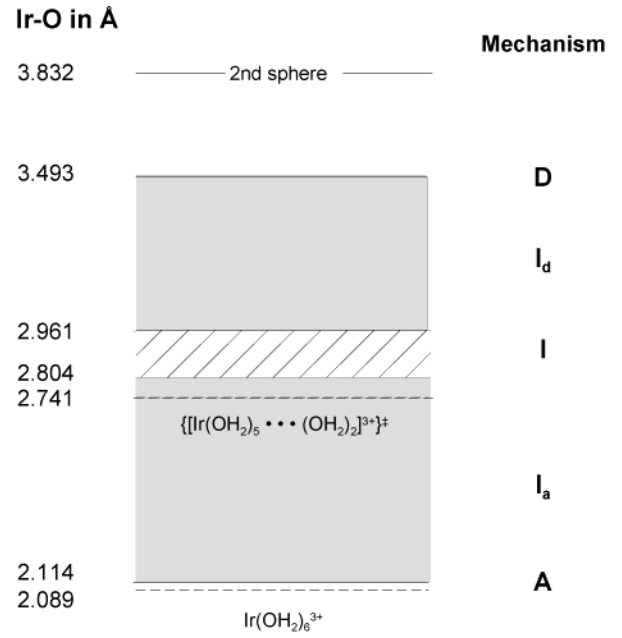

**Figure 5.** Water exchange on $Ir(OH_2)_6^{3+}$: relation between possible mechanisms and calculated oxygen−iridium distances of the reacting ligands at the corresponding transition states (in- - - - -: Ir−O bond length for the hexaquaion and the two exchanging water molecules in the transition state for the $I_a$ pathway).

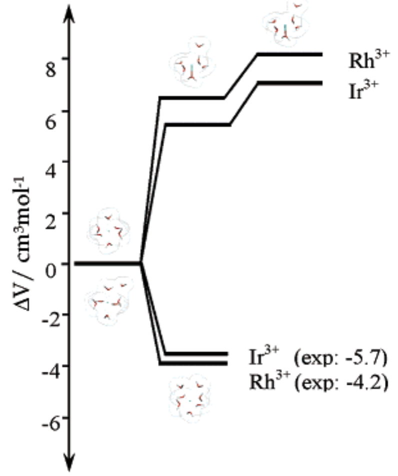

**Figure 6.** Volume changes (reactants−transition states−intermediates) for a dissociative D (top) and an interchange $I_a$ water exchange (bottom) on $Ir(OH_2)_6^{3+}$ and $Rh(OH_2)_6^{3+}$. In parentheses are experimental activation volumes.

for these two mechanisms is undoubtly in favor of the I mechanism, and very close to the experimental $\Delta G^{\ddagger}$ (298 K) value. Thus, the strong $Ir^{III}-O$ bonds constrain water exchange on $Ir(OH_2)_6^{3+}$ to proceed via an I mechanism, as already suggested for the $Rh(OH_2)_6^{3+}$.

It remains to assign the activation mode, keeping in mind that an associative mechanism is in principle disfavored for $t_{2g}^6$ species. First, we will use the variation of bond lengths on going to the transition state as previously done for $Rh(OH_2)_6^{3+}$ (Figure 5).[12] The Ir···O bond lengths of the two interchanging water molecules in the transition state $\{[Ir(OH_2)_5\cdots(OH_2)_2]^{3+}\}^{\ddagger}$ are slightly shorter than that calculated for an I pathway, allowing us to conclude at this stage an $I_a$ mechanism. In a second approach, to confirm the activation mode, we can consider the calculated volume changes on the basis of the Connolly surfaces for a dissociative and an interchange water exchange on $Ir(OH_2)_6^{3+}$ and on $Rh(OH_2)_6^{3+}$. For the D mechanism, the $\Delta V^{\ddagger}_{calc}$ values are +5.5 and +6.3 $cm^3\ mol^{-1}$, and for the I mechanism −3.5 and −3.9 $cm^3\ mol^{-1}$, respectively (Table 1, Figure 6). The agreement of the $\Delta V^{\ddagger}_{calc}$ with the experimental values (uncertainties ±1 $cm^3\ mol^{-1}$), and their negative signs, confirms the occurrence of an associative interchange water exchange on both $Ir^{3+}$ and $Rh^{3+}$ aquaions.

The $I_a$ mechanistic assignment for these two aquaions was questioned in the past,[40] and more generally, the use of the $\Delta V^{\ddagger}$ was open to debate,[14] primarily because the volume of activation can be, to some extent, affected by extension or compression of the nonparticipating ligand bond lengths on going to the transition state of an exchange process.[41] The water exchange process could follow a dissociative pathway and result in a net negative volume of activation due to the contraction of the five spectator ligands. In such a case, the change in volume of activation could no longer be the diagnostic tool for mechanistic characterization of water exchange reactions, but with the help of this theoretical study, it is now possible to give an answer to clarify this debate.

Indeed the calculation for the D mechanism shows an average shortening of 0.025 Å for the Ir−O bonds of the five spectator water molecules, from 2.089 to 2.064 Å at the transition state (Figure 2). Translating this contraction to $^5/_6$ of the volume of $Ir(OH_2)_6^{3+}$ (Connolly volume, $V = 95.83\ cm^3\ mol^{-1}$) gives a volume change of $-1.8\ cm^3\ mol^{-1}$. However this small value cannot explain an experimental $\Delta V^{\ddagger}$ value of $-5.7\ cm^3\ mol^{-1}$. Looking only at the calculated D mechanism, the $\Delta V^{\ddagger}_{calc}$ value of $+5.5\ cm^3\ mol^{-1}$ is thus made of a $-1.8\ cm^3\ mol^{-1}$ component for the bond contraction of the spectator ligands and $+7.3\ cm^3\ mol^{-1}$ component for the bond breaking of the leaving water molecule. Further, for the operating $I_a$ mechanism, contrarily to expectation, a shortening (0.013 Å), and not a lengthening, of the Ir−O spectator ligands bond lengths is observed. However, this shortening is definitely smaller as shown in Figure 3. Similar calculations as those performed above give a volume decrease of 0.9 $cm^3\ mol^{-1}$ during the activation, which leaves $-3.5 + 0.9 = -2.4\ cm^3\ mol^{-1}$ for the entry in the first coordination sphere of the seventh water molecule in a *cis* position with the leaving one, confirming an $I_a$ water exchange mechanism with a small a character.

## Conclusion

Experimental variable pressure studies on the two slowest water exchanging aquaions $Ir(OH_2)_6^{3+}$ and $Rh(OH_2)_6^{3+}$ have lead to negative activation volumes which were interpreted in terms of $I_a$ mechanisms for these two $t_{2g}^6$ aquaions. In this theoretical study, we show that the $I_a$ pathway with

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(40) Richens, D. T. *The Chemistry of Aquaions*; John Wiley: Chichester, England, 1997; p 465.

(41) Langford, C. H. *Inorg. Chem.* **1979**, *18*, 3288.

(42) Armstrong, R. S.; Beattie, J. K.; Best, S. P.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1973.

retention of the configuration of the spectator ligands is clearly preferred over the D pathway. This is due to the higher activation energy required for the dissociation of a water molecule, in particular for the most inert iridium(III) aquaion. Further, it is demonstrated that, for both mechanisms, the contribution to the volume of activation due to the changes in bond lengths between the Ir(III) and the spectator ligands is negligible: $-1.8$ $cm^3$ $mol^{-1}$ for the D, and $-0.9$ $cm^3$ $mol^{-1}$ for the $I_a$ mechanism. This finding is important and solves the debate about the interpretation of the activation volumes $\Delta V^{\ddagger}$. Finally, the agreement between the activation volumes $\Delta V^{\ddagger}_{calc}$ obtained using a simple model and level of calculations and experimental $\Delta V^{\ddagger}$ values unequivocally confirms the occurrence of an associative interchange water exchange mechanism $I_a$ with a small a character for the hexaaquaions of Rh(III) and Ir(III).

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**Supporting Information Available:** Listing of the total energies and atomic coordinates of all reactants/products, transition states, and pentacoordinated intermediates, and the corresponding Connolly volumes (Tables S1−S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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