ADVANCES IN Inorganic Chemistry

54

Edited by
R. van Eldik and C.D. Hubbard

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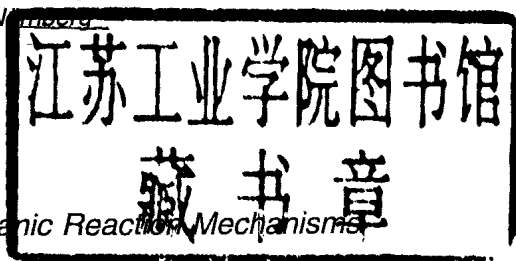
Including Bioinorganic Studies

EDITED BY

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VOLUME 54: Inorganic Reaction Mechanisms

ACADEMIC PRESS

An Imprint of Elsevier

Amsterdam   Boston   London   New York   Oxford   Paris
San Diego   San Francisco   Singapore   Sydney   Tokyo

Advances in

INORGANIC CHEMISTRY

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Volume 54

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PUBLISHER'S NOTE

This special volume of *Advances in Inorganic Chemistry*, with the thematic title Inorganic Reaction Mechanisms, is the first volume to be published under the auspices of the new editor, Professor Rudi van Eldik.

A Dutch national, Professor van Eldik studied chemistry at Potchefstroom University in South Africa, where he gained his D.Sc. in 1971. After a number of years working abroad, he was appointed Professor of Chemistry at Potchefstroom in 1979. In 1982 he received his Habilitation at the University of Frankfurt where he was Group Leader at the Institute for Physical Chemistry between 1980 and 1986. From 1987 to 1994 he was Professor of Inorganic Chemistry at the University of Witten/Herdecke, Germany and was then appointed to his present position as Professor of Inorganic and Analytical Chemistry at the University of Erlangen-Nürnberg in Germany. In the intervening years he has travelled widely, being a Visiting Professor at the University of Utah in the USA, the University of Canterbury in New Zealand, Ben Gurion University in Israel and at the moment is Wilsmore Visiting Professor at the University of Melbourne in Australia.

A prolific author, Professor van Eldik has been responsible for some 580 papers in refereed journals, and four books as editor or co-editor. His current research intrests are the application of high pressure techniques in mechanistic studies; metal-catalyzed autoxidation processes; and bioinorganic studies. As such he is eminently qualified to edit the prestigious *Advances in Inorganic Chemistry.* We are confident that he is a worthy successor to Professor Geoff Sykes and that he will maintain the high standards for which the series is known.

PREFACE

I am especially honoured to have been ·appointed the Editor of *Advances in Inorganic Chemistry*, and to be associated with a highly cited, very successful series. The series began in 1959, edited by H.J. Emeléus and A.G. Sharpe, and at that time included reviews on Radiochemistry. With Volume 31, Professor A.G. Sykes assumed the editorship and extended the area of interest to include bioinorganic studies. He prefaced that issue with an outline of his views on the aims of the series, and (paraphrasing) he intended to continue to provide a forum for scholarly and critical reviews by recognized experts, rather than seeking to catalogue each and every event. Those opinions and other comments were very appropriate then and remain so, now and in the future.

Contributions will be solicited by the editor, who will also be guided by the Editorial Advisory Board. Issues on thematic topics will in general involve a co-editor as a specialist in that particular field. Suggestions for subjects for reviews in the future will be welcome at any time. Of particular interest will be reviews of rapidly developing areas that do not necessarily fit into traditional subject sub-areas, thus appealing to newer readers and research colleagues. It is felt that a presentation of diverse topics will assist in creative thinking and help to ensure that the overall subject of Inorganic Chemistry continues to develop and thrive. In this respect, I would like to welcome the new Advisory Board members and will look forward to interacting with them.

To honour the accomplishments of Professor Geoff Sykes, both in his own research, principally in mechanistic studies in Inorganic and Bioinorganic Chemistry, and as editor of this series, the present volume on Inorganic Reaction Mechanisms is dedicated to him. The Publisher's note in Volume 53 referred to the high impact factor as a reflection of the high standards set and the quality of the contributing authors. I echo these comments and personally acknowledge Professor Sykes'

significant contribution to the success of the series. I am delighted and
feel privileged to succeed illustrious editors and will endeavour to
match their high standards.

For my first volume as Editor, I have invited Professor Colin D.
Hubbard (University of Erlangen-Nürnberg, Erlangen, Germany and
University of New Hampshire, Durham, NH, USA) as co-editor.
Professor Hubbard studied chemistry at the University of Sheffield, and
obtained his PhD with Ralph G. Wilkins. Following post-doctoral work
at MIT, Cornell University and University of California in Berkeley, he
joined the academic staff of the University of New Hampshire, Durham,
where he became Professor of Chemistry in 1979. His interests cover the
areas of high-pressure chemistry, electron transfer reactions, proton tun-
nelling and enzyme catalysis.

The first chapter by F.A. Dunand, L. Helm and A.E. Merbach is a com-
prehensive account of the mechanism of solvent exchange processes.
Metal complex formation can be controlled by solvent exchange. This
topic, as well as ligand substitution in general, form the subject of the
second chapter by J. Burgess and C.D. Hubbard. Following this, J.H.
Espenson describes 'Oxygen Transfer Reactions: Catalysis by Rhenium
Compounds'. The fourth chapter by P.C. Ford, L.E. Laverman and J.M.
Lorkovic is an account of the reaction mechanisms of nitric oxide with
biologically relevant metal centers. In chapter 5, U. Fekl and K.I.
Goldberg discuss 'Platinum Involvement in Homogeneous Hydrocarbon
C–H Bond Activation and Functionalization'. Chapter 6 by M.H. Hall
and H.-J. Fan is titled 'Density Functional Studies of Iridium Catalyzed
Alkane Dehydrogenation'. 'Recent Advances in Electron Transfer
Reactions' are reported by D.M. Stanbury. The final chapter by I. Fábián
and V. Csordás is on 'The Kinetics and Mechanism of Metal Ion
Catalyzed Autoxidation Reactions'. I thoroughly believe that these contri-
butions cover the present advances accomplished in the general area of
Inorganic Reaction Mechanisms.

Rudi van Eldik
University of Erlangen-Nürnberg
Germany
December 2002

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SOLVENT EXCHANGE ON METAL IONS

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I. Introduction

A. GENERAL ASPECTS

Solvent exchange reactions on metal cations are among the most
simple chemical reactions: a solvent molecule situated in the first coordi-
nation shell of the ion is replaced by another one, normally entering
from the second shell. They are generally considered as fundamental
reactions for metal ions in solution, since they constitute an important
step in complex-formation reactions on metal cations. The reaction is

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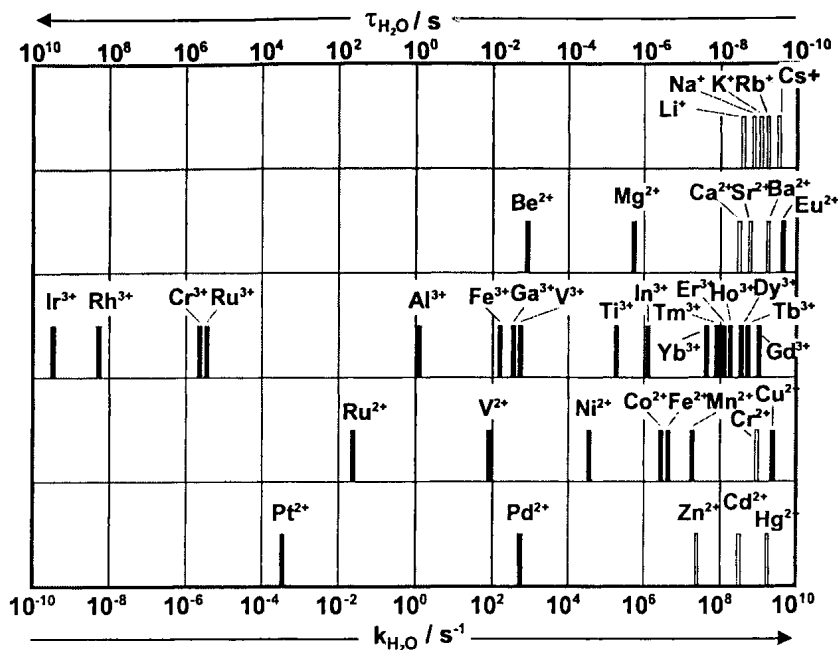
FIG. 1. Mean lifetimes of a particular water molecule in the first coordination sphere of a given metal ion, τ_{H_2O}, and the corresponding water exchange rate constants, k_{H_2O} at 298 K. The filled bars indicate directly determined values, and the empty bars indicate values deduced from ligand substitution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

symmetrical: reactants and reaction products are identical, which has important drawbacks in the determination of the rate constants.

The rates of solvent exchange vary widely with the nature of the cation and, to a lesser extent, with that of the solvent. As an example Fig. 1 shows that k_{H_2O}, the exchange rate constant for water molecules, covers nearly 20 orders of magnitude. At the "slow end" of the lability scale the mean life time of a water molecule in the 1st coordination shell of $[Ir(H_2O)_6]^{3+}$, τ_{H_2O} ($=1/k_{H_2O}$) is about 290 years (1), whereas at the other extreme the shortest mean life time is 2×10^{-10} s ($=200$ ps) directly measured on $[Eu(H_2O)_7]^{2+}$ (2). Variation of the rate constant with solvent on the same metal ion is less pronounced and generally below 2 orders of magnitude. Strong back-bonding from the metal to solvent molecules, however, can slow down the exchange process by several orders of magnitude, as observed for example for $[Ru(MeCN)_6]^{3+}$ (3). It is therefore convenient to divide the discussion of solvent exchange into categories of metal ions.

The first category includes the main group ions, which exhibit in general, for a given ionic charge, increasing exchange rate constants, k_{ex}, with increasing ionic radius. This is nicely illustrated by the water exchange on Al^{3+}, Ga^{3+} and In^{3+}, all being six-coordinate, with a rate increase of more than 6 orders of magnitude. Solvent exchange on mono-valent alkali and large divalent alkali-earth ions is very fast and the exchange rate constants can only be deduced from complex-formation reactions (4,5).

The second category is the d-transition metal ions. Their solvent exchange properties are strongly influenced by the electronic occupancy of their d orbitals. This is best illustrated by the 1st row transition metal ions. On the basis of their ionic radii, r_M, they should all show labilities similar to Zn^{2+} for the divalent ions and similar to Ga^{3+} for the trivalent ones. However, the water exchange rates vary by 7 and 15 orders of magnitude, respectively, depending largely on the electronic configuration of the metal ion. Within this category, square-planar complexes constitute a special sub-category.

The third category is the high coordination number lanthanides and actinides. The trivalent lanthanides show a decrease in r_M with the progressive filling of the 4f orbitals, called the lanthanide contraction. Since the 4f orbitals are shielded by the filled 5s and 5p orbitals, the electronic configuration has no remarkable effect and therefore the variation in r_M and an eventual change in coordination number and geometry determine the lability of the 1st coordination shell.

Solvent exchange reactions have been reviewed several times in the last 10 years. A comprehensive review by Lincoln and Merbach was published in this series in 1995 (6). More recent reviews focused more on high pressure techniques for the assignment of reaction mechanisms (7–9) or on water exchange (10). This review is a follow up of the exhaustive Lincoln and Merbach review (6). The main features of solvent exchange on metal ions will be pointed out, taking into account developments and new results from the last 10 years.

B. EXPERIMENTAL METHODS

Only a few experimental techniques are available to measure solvent exchange rate constants directly. Nuclear magnetic resonance (NMR) spectroscopy has shown the widest range of application. Most exchange rate constants given in this review were determined by NMR using a variety of specific methods. A common method is the observation of NMR lineshape (11). If the exchange rate constant is in the range defined by the natural linewidth of the NMR resonance and there is a chemical

shift difference between resonance signals of bulk solvent and solvent molecules in the 1st coordination shell (both in $\mathrm{rad\,s^{-1}}$), k_{ex} can be directly determined from the NMR spectrum. This means that rates in the order of several $\mathrm{s^{-1}}$ can be measured by ^{1}H or ^{13}C NMR as well as rates of the order of $10^6\,\mathrm{s^{-1}}$ if chemical shift differences are large due to paramagnetic effects. Even faster exchange rates can be determined using methods based on relaxation rate measurements. Using these methods, the fastest rate measured by NMR up to now is $\sim 5 \times 10^9\,\mathrm{s^{-1}}$ (2). Relatively slow exchange reactions from k_{ex} 0.1 to $10\,\mathrm{s^{-1}}$ can be followed using magnetization transfer experiments. By exciting spins on a chemical site, well defined by its NMR signal, and observing how this excitation is transferred by the chemical reaction to another site, reaction rates can be obtained if the reaction proceeds faster than nuclear spin relaxation (12,13).

Very slow reactions can be followed by isotopic labeling techniques. The solvent molecules in the 1st shell of the metal ion or the bulk solvent may be labeled either using stable isotopes as for example ^{2}H, ^{13}C, ^{15}N or ^{17}O or either radioactive isotopes as ^{14}C or ^{3}H. The exchange of the labeled molecules can be followed with various techniques like NMR, mass spectroscopy, or radiation counting after precipitation. There is in principle no lowest limit of k_{ex} to be measured by the labeling method; samples can be stored in a thermostated bath for months and transferred from time to time into a NMR spectrometer to record the progress of the reaction. To accelerate the reaction, measurements can be performed at high temperature. Water exchange on the extremely slow $[\mathrm{Ir(H_2O)_6}]^{3+}$ was measured at temperatures from 358 to 406 K and the value at 298 K was then extrapolated from these data (1).

Measuring very fast solvent exchange rates is very difficult, especially on diamagnetic ions where the NMR technique described above cannot be applied. Some information on the dynamics of water protons in aqueous ionic solution is available from high-resolution incoherent quasi-elastic neutron scattering (IQENS). Based on differences of translational diffusion constants for bulk and bound water, this technique allows one to establish a time-scale for ion-water proton binding (14). From the experimental data it can be decided if the binding time $\tau_{\mathrm{H_2O}}$ is short ($\leq 10^{-10}\,\mathrm{s}$) or long ($\geq 5 \times 10^{-9}\,\mathrm{s}$) on the IQENS observation timescale (15). Between these two limits binding times can be estimated from the IQENS spectra. Very fast water exchange rates can be estimated from rates of complex formation on the aqua ions, measured by ultra sound absorption or temperature-jump techniques (4,5). If the formation of the inner sphere complex involves the movement of a ligand from the second to the first coordination sphere and this is the rate-determining

step in the complex-formation reaction, then this rate can be considered to be close to the water exchange rate.

Measuring the pressure dependence of the exchange rate constant leads to activation volumes, $\Delta V^{\ddagger}$, and this technique has become a major tool for the mechanistic identification of solvent exchange mechanisms (8,16,17). In the last 25 years high-pressure, high-resolution NMR probes were developed which allow the application of all NMR techniques described to pressures up to several hundreds of mega Pascals (18).

C. CLASSIFICATION OF MECHANISMS

The mechanistic classification generally accepted for ligand substitution reactions was proposed by Langford and Gray in 1965 (19). This classification was often discussed in the literature and its principles are only summarized here for convenience.

$$MX_n \; \underset{+X}{\overset{-X}{\rightleftarrows}} \; \{MX_{n-1}\} \; \underset{-Y}{\overset{+Y}{\rightleftarrows}} \; MX_{n-1}Y \quad (\mathbf{D} = \text{dissociative}) \qquad (1)$$

$$MX_n \; \underset{-Y}{\overset{+Y}{\rightleftarrows}} \; \{MX_nY\} \; \underset{+X}{\overset{-X}{\rightleftarrows}} \; MX_{n-1}Y \quad (\mathbf{A} = \text{associative}) \qquad (2)$$

$$MX_n \cdots Y \; \overset{\longrightarrow}{\rightleftarrows} \; MX_{n-1}Y \cdots X \quad (\mathbf{I} = \text{interchange}) \qquad (3)$$
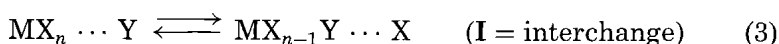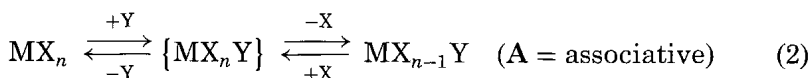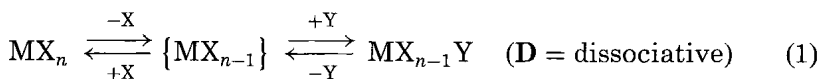
Langford and Gray divided substitution reactions into three categories of stoichiometric mechanisms: *associative* (**A**) where an intermediate of increased coordination number is inferred, or *dissociative* (**D**) where an intermediate of reduced coordination number is inferred, and *interchange* (**I**) where there is no kinetically detectable intermediate [Eq. (3), $MX_n \cdots Y$ represents an outer-sphere complex]. They further distinguish two categories of *intimate mechanisms*: mechanisms with an associative activation mode (**a**) and mechanism with a dissociative activation mode (**d**). In the first case the reaction rate is sensitive to the nature of the entering group whereas in the second case the reaction rate is not sensitive to the variation of the entering group but to the nature of the leaving group.

All **A** mechanisms must be associatively and all **D** mechanisms must be dissociatively activated. The interchange mechanisms (**I**) include a continuous spectrum of transition states where the degree of bond-making between the entering ligand and the complex ranges from very substantial ($\mathbf{I_a}$ mechanism) to negligible ($\mathbf{I_d}$ mechanism) and inversely

for bond-breaking (*16*). For a solvent exchange reaction, the forward and backward reaction coordinates must be symmetrical.

How can mechanisms be assigned to solvent exchange reactions? The rate law for solvent exchange reaction can be determined using an inert diluent. Unfortunately such a diluent does not exist for all solvents: there is no inert diluent known for water for example. The variation of the enthalpy and entropy of activation, obtained from variable temperature experiments, within a series of similar ligand substitution systems can give a guide to a mechanistic changeover. Thus **d**-activated reactions tend to have greater $\Delta H^{\ddagger}$ values than do **a**-activated reactions, and $\Delta S^{\ddagger}$ tends to be positive for **d**- and negative for **a**-activated reactions. However, the magnitudes of the contributions to these two parameters arising from interactions that occur beyond the 1st coordination shell can be uncertain; hence the determination of $\Delta S^{\ddagger}$ is often prone to systematic errors. By the choice of adequate conditions, the precision of measurement of $\Delta V^{\ddagger}$ is high and there is a direct relationship between its sign and the increase or decrease of the rate constant with pressure. Therefore, establishment of the dependence of the exchange rate constant on pressure, leading to volumes of activation $\Delta V^{\ddagger}$, provides a major tool for the experimental identification of solvent exchange mechanisms (*20–22*).

D. THE VOLUME OF ACTIVATION

The volume of activation, $\Delta V^{\ddagger}$, is defined as the difference between the partial molar volumes of the transition state and the reactants. It is related to the pressure variation of the rate constant by Eq. (4):

$$\left(\frac{\partial \ln(k)}{\partial P}\right)_T = -\frac{\Delta V^{\ddagger}}{RT} \tag{4}$$

Assuming that $\Delta V^{\ddagger}$ is slightly pressure dependent leads to the approximate Eq. (5),

$$\ln(k_P) = \ln(k_0) - \frac{\Delta V_0^{\ddagger} P}{RT} + \frac{\Delta \beta^{\ddagger} P^2}{2RT} \tag{5}$$

where k_P and k_0 are the rate constants at pressures P and 0, respectively, $\Delta V_0^{\ddagger}$ is the activation volume at zero pressure and $\Delta \beta^{\ddagger}$ is the compressibility coefficient of activation. For solvent exchange the quadratic term in Eq. (5) is very often small compared to the linear one for pressures generally applied in kinetic studies (typically 0–150 MPa) and therefore $\Delta V^{\ddagger} \cong \Delta V_0^{\ddagger}$.