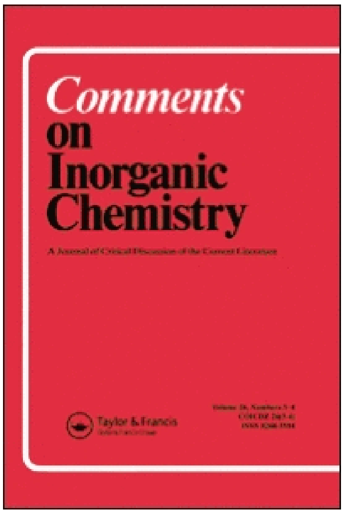


Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

High Pressure Kinetics. A Decisive Dimension in Mechanistic Studies of Inorganic Reactions

Rudi Van Eldik[a]; André E. Merbach[b]
[a] Institut für Anorganische Chemie, Universität Witten/Herdecke, Witten, Germany [b] Institut de Chimie Minérale et Analytique, Universitè de Lausanne, Lausanne, Switzerland

To cite this Article Van Eldik, Rudi and Merbach, André E.(1992) 'High Pressure Kinetics. A Decisive Dimension in Mechanistic Studies of Inorganic Reactions', Comments on Inorganic Chemistry, 12: 6, 341 — 378
To link to this Article: DOI: 10.1080/02603599208055169
URL: http://dx.doi.org/10.1080/02603599208055169

High Pressure Kinetics. A Decisive Dimension in Mechanistic Studies of Inorganic Reactions

RUDI VAN ELDIK
Institut für Anorganische Chemie,
Universität Witten/Herdecke,
Stockumer Strasse 10,
5810 Witten, Germany

ANDRÉ E. MERBACH
Institut de Chimie Minérale et Analytique,
Université de Lausanne,
3, Place du Château,
1005 Lausanne, Switzerland

Received September 13, 1991

An account of our most recent studies on the application of high pressure kinetic techniques in mechanistic studies of inorganic reactions is presented. The investigated reactions include substitution, addition, insertion, elimination, electron-transfer, photo-induced substitution, and irradiation-induced processes. In addition some data for typical bioinorganic systems are reported and future perspectives are described. The account clearly demonstrates that high pressure kinetics adds a further dimension to mechanistic studies of chemical reactions in solution.

Key Words: *high pressure kinetics, mechanistic studies, volumes of activation, inorganic, organometallic, and bioinorganic reactions, thermal and photochemical processes*

INTRODUCTION

Our research groups have over the past decade been most intensively involved with the application of high pressure kinetic tech-

---

Comments Inorg. Chem.
1992, Vol. 12, No. 6, pp. 341–378
Reprints available directly from the publisher
Photocopying permitted by license only

niques in the study of inorganic and organometallic reaction mechanisms in solution.[1-7] This has resulted in a vigorous development of various experimental techniques that enable the application of pressure as a kinetic parameter on a routine basis.[8] In this way we and others have added a further dimension to mechanistic studies of inorganic reactions in solution by introducing pressure as an important physical variable in addition to the more commonly employed variable temperature. The results reported during this period are very encouraging and motivated us to present a state of the art account on this topic. We would like to demonstrate the advantages of this technique, to report some of the most exciting results obtained using this technique, and to focus on present and possible future activities in this area. Although we will mainly present examples from our own investigations, there are numerous reports in the literature on activities from other groups as summarized in a number of recent reviews.[1-9] In these, a complete coverage of all the original contributions and earlier reviews that have appeared in this area is made.

It is our personal attitude that when dealing with mechanistic studies in general it is essential to investigate as many chemical (concentration, pH, solvent, ionic strength) and physical (temperature, pressure) variables as possible in order to obtain as much indirect information as possible on the nature of the underlying reaction mechanism. Only then can the suggested mechanism come close to the "real" mechanism, which is a goal set by many kineticists but not always accomplished. It is therefore in our opinion essential to include pressure as a standard physical variable in mechanistic studies dealing with chemical reactions in solution.

EXPERIMENTAL TECHNIQUES

Pressure can be varied over a wide range from a few to hundreds of kilobars (1 kbar = 100 MPa) depending on the technique employed and phenomenon investigated. For kinetic studies in coordination chemistry the pressure range is usually limited to 400 MPa. Such pressures can significantly affect the value of a rate or equilibrium constant, which forms the basis of all treatments of activation and reaction volume data. It is important to note that very high pressures are not needed since activation and reaction volumes are determined from the pressure dependence of rate and equilibrium constants at zero pressure. The idea of performing experiments at high pressure usually invokes a fear of complicated, dangerous and expensive instrumentation. However, the instrumentation employed is relatively simple, involves minimal danger since the pressure is created via the mechanical compression of liquids, and in some cases is commercially available. Various instruments for the study of slow and fast reactions including flow systems and relaxation techniques have been developed. A detailed discussion on these is presented in two recent reviews.[8,9] The techniques involve stopped-flow, T-jump, P-jump, NMR, ESR and pulsed-laser instrumentation. In the case of the high resolution variable pressure NMR measurements, recent developments include the application of magnetization transfer and 2D techniques to study ligand exchange processes.[9] They cover a kinetic time range from hours and days to nano- and picoseconds. Some of the equipment is very versatile and transportable.[10] Most of the instruments are usually home-made and constructed by the instrument shops of the laboratories involved. For more detailed information we advise those interested to contact the individual groups directly.

The tremendous progress made in the development of fast reaction techniques and the handling of air and oxygen sensitive samples[11] at elevated pressure has stimulated the progress made in inorganic/organometallic mechanistic studies. During the period 1977 to 1987 over a thousand sets of data (i.e., volumes of activation) were reported for such reactions.[3] Volumes of activation exhibit some important advantages over entropies of activation: they can be determined more accurately; their interpretation is less difficult; their magnitude can be visualized or estimated with the help of models; their values can be correlated with partial molar volumes of reactant and product species in the ground state to construct a reaction volume profile.

INVESTIGATED REACTIONS

The fundamental principles involved in high pressure kinetics, the determination of activation and reaction volumes, the construction of reaction volume profiles and the interpretation of such data have been treated in detail elsewhere.[1-3,8] The interpretation of the pressure dependence of a rate constant is based on a simplified version of the transition state theory, which does not take the dynamics of the reactant–solvent interaction into account. This simplification usually applies to nondiffusion-controlled processes and has been adopted in the examples presented in this account. In the following sections, typical examples of thermal and photochemical substitution and electron-transfer reactions of inorganic and organometallic complexes are presented. This is followed by a report on radiation induced reactions and bioinorganic systems. Finally, a short account on present and future activities in our groups and an evaluation of the method in the form of final conclusions is presented.

a. Substitution Reactions

During the last two decades, the volume of activation has become a well established criterion to assess the mechanisms of substitution reactions. For a general ligand substitution reaction (1),

$$\mathrm{ML_nX} + \mathrm{Y} \rightarrow \mathrm{ML_nY} + \mathrm{X} \qquad (1)$$

where X is the leaving and Y the entering ligand, there are three simple pathways[12]: (i) the dissociative (D) process, with an intermediate of lower coordination number; (ii) the associative (A) process, with an intermediate of higher coordination number; (iii) the interchange (I) process, in which no intermediate of lower or higher coordination number is involved. The latter possibility is further subdivided into two types: associative interchange ($\mathrm{I_a}$) or dissociative interchange ($\mathrm{I_d}$), depending on whether bond formation or bond breakage is the primary process during the interchange of the ligands. In general the volume of activation ($\Delta V^{\#}$) for such processes should reflect the nature of the substitution mechanism since $\Delta V^{\#}$ consists of two contributions[3,5]: an intrinsic component $\Delta V^{\#}_{\mathrm{intr}}$ resulting from changes in bond lengths and bond angles, and a solvational component $\Delta V^{\#}_{\mathrm{solv}}$ resulting from changes in electrostriction. Fortunately, for solvent- and neutral ligand-exchange reactions, i.e., where no net chemical reaction occurs, changes in electrostriction will be negligible and $\Delta V^{\#} \approx \Delta V^{\#}_{\mathrm{intr}}$. Thus the volume of activation will be a direct measure of the degree of bond formation or bond breakage in the transition state, keeping in mind that some extension or compression of the non-participating ligand (L) bond lengths occurs during such processes. A continuous spectrum of transition state configurations can be envisaged, ranging from a very compact, highly associative one (large negative $\Delta V^{\#}$), to a very expanded, highly dissociative one (large positive $\Delta V^{\#}$) as illustrated in Fig. 1 for a symmetrical reaction.

Typical results for solvent exchange on some diamagnetic d^0 and d^{10} trivalent cations are reported in Table I. For Al^{3+} and Ga^{3+} the $\Delta V^{\#}$ values in non-aqueous solvents together with the first-order rate laws are typical for a D mechanism, whereas for Sc^{3+} and In^{3+} the $\Delta V^{\#}$ values, together with the second-order rate laws, are typical for an associative (A or I_a) mechanism. For water exchange on Al^{3+} and Ga^{3+} the $\Delta V^{\#}$ values are well below that expected for a limiting D mechanism, and it is concluded that an I_d mechanism operates. The solvent exchange reactions of first row high spin trivalent transition metal ions are characterized by $\Delta V^{\#}$ values that exhibit a definite trend across the series (Table II):

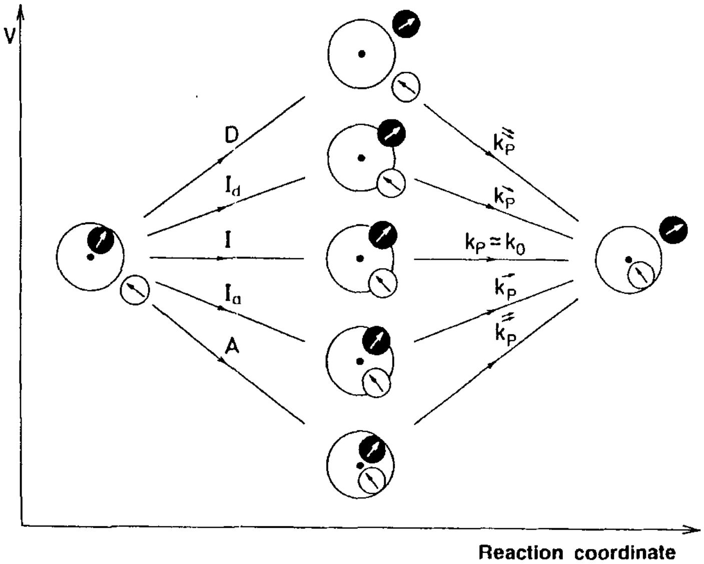


FIGURE 1 Volume profiles for solvent exchange mechanisms.

TABLE I

Kinetic parameters for solvent exchange on diamagnetic trivalent cations in CD_3NO_2 as diluent (Ref. 5)

	r_i pm	k_1^{298} s^{-1}	k_2^{298} s^{-1} mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J K^{-1} mol^{-1}	$\Delta V^{\#}$ cm^3 mol^{-1}	Mechanism
$Al(H_2O)_6^{3+a}$	54	1.29		84.7	+41.6	+5.7	I_d
$Al(DMSO)_6^{3+}$		0.30		82.6	+22.3	+15.6	D
$Al(DMF)_6^{3+}$		5×10^{-2}		88.3	+28.4	+13.7	D
$Al(TMPA)_6^{3+}$		0.78		85.1	+38.2	+22.5	D
$Ga(H_2O)_6^{3+a}$	62	4.0×10^2		67.1	+30.1	+5.0	I_d
$Ga(DMSO)_6^{3+}$		1.87		72.5	+3.5	+13.1	D
$Ga(DMF)_6^{3+}$		1.72		85.1	+45.1	+7.9	D
$Ga(TMPA)_6^{3+}$		6.4		76.5	+27.0	+20.7	D
$Sc(TMPA)_6^{3+a}$	75	736	85	34.1	−75.6	−23.8	A, I_a
$Sc(TMPA)_6^{3+}$			39	21.2	−143.5	−18.7	
$In(TMPA)_6^{3+}$	80		7.6	32.8	−118	−21.4	A, I_a

[a] In neat solvent.

TABLE II

Volumes of activation (cm^3 mol^{-1}) for solvent S exchange on MS_6^{3+} of the first row transition metal series[a] (Ref. 7).

M^{3+}	Sc	Ti	V	Cr	Fe	Ga
r_i/pm	75	67	64	61	64	62
	t_{2g}^0	t_{2g}^1	t_{2g}^2	t_{2g}^3	$t_{2g}^3e_g^2$	$t_{2g}^6e_g^4$
H_2O		−12.1	−8.9	−9.6	−5.4	+5.0
DMSO			−10.1	−11.3	−3.1	+13.1[b]
DMF				−6.3	−0.9	+7.9[b]
TMP	−21.3					+20.7[b]

[a] By NMR except for Cr^{3+} by isotopic labelling.
[b] In CD_3NO_2 as diluent.

$\Delta V^{\#}$ becomes significantly more positive along the series. This trend is interpreted in terms of a changeover in mechanism from associative for the larger to dissociative for the smaller cations. A similar changeover in mechanism was found for solvent exchange on high spin first row divalent transition metal ions in water (Fig. 2), methanol and acetonitrile (Table III). The values indicate that

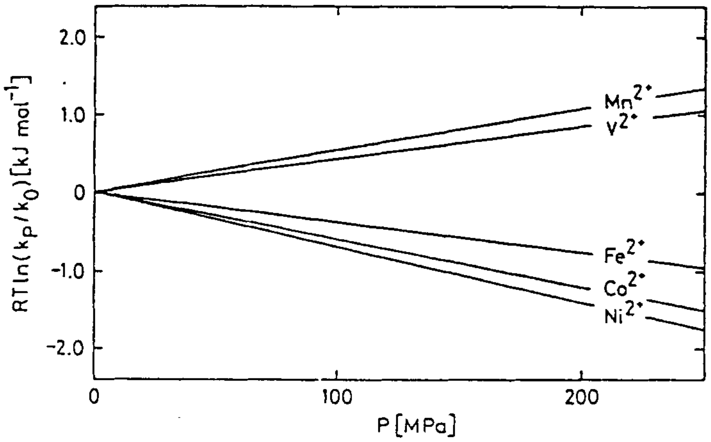


FIGURE 2 Influence of pressure on the water exchange rate on octahedral high spin divalent first row transition metal ions (Ref. 6).

TABLE III

Volumes of activation ($\mathrm{cm^3\ mol^{-1}}$) for solvent S exchange on MS_6^{2+} of the first row transition metal series by NMR (Ref. 7).

M^{2+}	V	Mn	Fe	Co	Ni	Cu
r_i/pm	79	83	78	74	69	(73)[a]
	t_{2g}^3	$t_{2g}^3e_g^2$	$t_{2g}^4e_g^2$	$t_{2g}^5e_g^2$	$t_{2g}^6e_g^2$	($t_{2g}^6e_g^3$)
H_2O	−4.1	−5.4	+3.8	+6.1	+7.2	
MeOH		−5.0	+0.4	+8.9	+11.4	+8.3
MeCN		−7.0	+3.0	+8.1	+8.5[c]	
DMF		+2.4[d]	+8.5	+9.2	+9.1	
NH_3[b]					+5.9	

[a] Effective ionic radius.

[b] In 15 M aqueous NH_3.

[c] Recent values[13] obtained for a series of nitriles by ^{14}N NMR are the following: +12.0 for acetonitrile, +13.7 for propionitrile, +13.1 for butyronitrile, +12.4 for isobutyronitrile, +14.4 for valeronitrile and +13.1 for benzonitrile.

[d] Reported in Refs. 14–16.

the mechanism for solvent exchange progressively changes from I_a for the early elements to I_d for the later ones, and can be explained by the progressive filling of the d orbitals and the decrease in the ionic radii along the series. This systematic trend can be visualized with the aid of a two-dimensional More O'Ferral plot[6] presented in Fig. 3. The sum of the coordinates of each point along a trajectory represents the change in volume to reach that point. The $\Delta V^{\#}$ value is obtained at the intersection with the dashed line. A limiting $\Delta V^{\#}$ value of 13 $cm^3\ mol^{-1}$ was chosen in Fig. 3. The small positive $\Delta V^{\#}$ found for DMF exchange on Mn^{2+} (determined by three independent laboratories[14-16]) indicates that steric hindrance on the hexasolvates prevents the associative substitution mode even for the largest metal center in this bulky solvent.

The above quoted examples clearly demonstrate the sensitivity of $\Delta V^{\#}$ towards changes in the solvent exchange mechanism for octahedral metal ions along specific series in the periodic table. Such data can also distinguish between the solvent exchange mechanism for $M(H_2O)_6^{3+}$ and its conjugate base $M(H_2O)_5OH^{2+}$ as indicated in Table IV. The higher reactivity of the hydroxo complexes is accompanied by a more dissociative character (more pos-

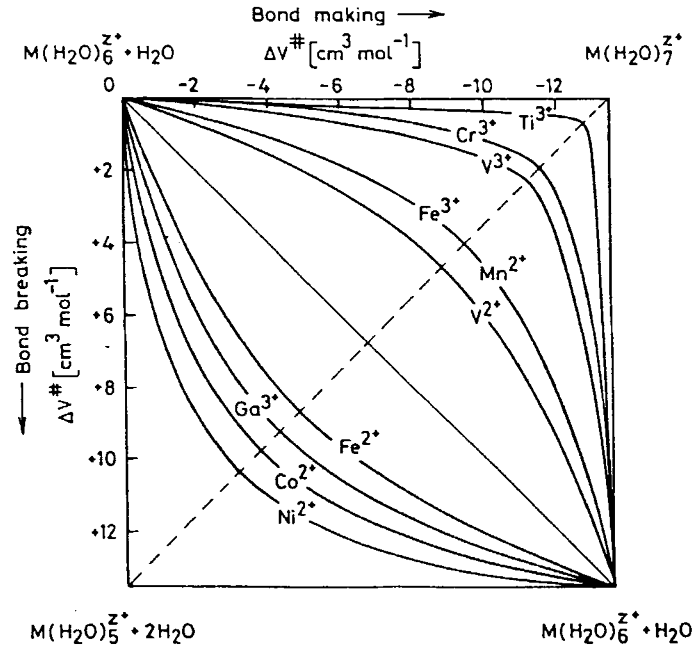


FIGURE 3 Bond making and bond breaking contributions to the volumes of activation for water exchange on $M(H_2O)_6^{z+}$ (Ref. 6).

TABLE IV

Rate constants and activation parameters for water exchange on some hexaaqua and monohydroxypentaaqua metal ions (Ref. 9).

M^{3+}	k^{298} s^{-1}	k_{OH}/k	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J K^{-1} mol^{-1}	$\Delta V^{\#}$ cm^3 mol^{-1}	pK_a	Mechanism
Ga^{3+}	4.0×10^2	275	67.1	+30.1	+5.0	≈3.9	I_d
$Ga(OH)^{2+}$	1.1×10^5		58.9	–	+6.2		I_d
Fe^{3+}	1.6×10^2	750	64.0	+12.1	−5.4	2.9	I_a
$Fe(OH)^{2+}$	1.2×10^5		42.4	+5.3	+7.0		I_d
Cr^{3+}	2.4×10^{-6}	75	108.6	+11.6	−9.6	4.1	I_a
$Cr(OH)^{2+}$	1.8×10^{-4}		110.0	+55.6	+2.7		I
Ru^{3+}	3.5×10^{-6}	170	89.8	−48.2	−8.3	2.7	I_a
$Ru(OH)^{2+}$	5.9×10^{-4}		95.8	+14.9	+0.9		I
Rh^{3+}	2.2×10^{-9}	19100	131.2	+29.3	−4.2	3.5	I_a
$Rh(OH)^{2+}$	4.2×10^{-5}		103.0	–	+1.3		I

itive $\Delta V^{\#}$) for water exchange. In a similar way the solvent- and ligand-exchange reactions of four- and five-coordinate complexes can be characterized by the associated $\Delta V^{\#}$ values.[3,5,9] The majority of square planar complexes undergo ligand exchange by a pathway that involves associative behaviour, and the corresponding $\Delta V^{\#}$ values are significantly negative (see Table V). Introducing steric hindrance on the diethylenetriamine (dien) ligand substantially decreases the water-exchange rate constant but does not change the basic nature of the associative exchange process. For the last entries in Table V the exchange of Me_2S and Me_2SO is characterized by positive volumes of activation, which show beyond doubt that the presence of the Pt–C bond causes a changeover in mechanism to a dissociatively activated process. These examples clearly demonstrate the importance of steric versus electronic effects.

In many ligand substitution reactions the product species differ from the reactant species, i.e., a non-symmetrical substitution process, and the overall reaction volume is usually not zero as in the case of solvent- and ligand-exchange processes. However, mechanistic similarities are expected to occur for ligand substitution

TABLE V

Selected exchange rate constants and activation parameters for solvent and ligand exchange on square planar Pd^{2+} and Pt^{2+} (Ref. 9).

Complex	Solvent	k_{ex}^{298a}	$\Delta H^{\#}$/kJ mol^{-1}	$\Delta S^{\#}$/J K^{-1} mol^{-1}	$\Delta V^{\#}$/cm^3 mol^{-1}	Mechanism
$[Pd(H_2O)_4]^{2+}$	water	10[b]	49	-60	-2.2	I_a, A
$[Pd(dien)H_2O]^{2+}$	water	93[b]	38	-80	-2.8	I_a, A
$[Pd(Me_5dien)H_2O]^{2+}$	water	3.4[b]	62	-27	-7.2	I_a, A
$[Pd(Et_5dien)H_2O]^{2+}$	water	5.3×10^{-2}[b]	63	-58	-7.7	I_a, A
trans-$[Pd(Me_2S)_2Cl_2]$	C_6H_5CN	197[b]	38	-73	-5.9[d]	I_a, A
$[Pt(H_2O_4]^{2+}$	water	7.1×10^{-6}[b]	90	-43	-4.6	I_a, A
$[Pt(Me_2SO)_2(Me_2SO)_2]^{2+}$[c]	CH_3NO_2	3.2×10^{3}[b]	33	-62	-2.5	I_a, A
$[Pt(Me_2SO)_2(Me_2SO)_2]^{2+}$[f]	CH_3NO_2	2[b]	47	-74	-6	I_a, A
cis-$[PtPh_2(Me_2S)_2]$	benzene	0.21[c,g]	101[g]	$+42$[g]	$+4.7$	D
cis-$[PtPh_2(Me_2SO)_2]$	benzene	1.24[c,g]	64[g]	-67[g]	$+5.5$[h]	D
cis-$[PtMe_2(Me_2S)_2]$	benzene	1.38[c,g]	90[g]	$+21$[g]		D
cis-$[PtMe_2(Me_2SO)_2]$	benzene	0.60[c,g]	85[g]	-3[g]		
	benzene	1.12[c]	84	-1	$+4.9$	D

[a] All values refer to the exchange of one particular solvent molecule.

[b] In m^{-1} s^{-1}.

[c] In s^{-1}.

[d] Intrinsic $\Delta V^{\#}$ in an hypothetical nonsolvating solvent.

[e] O-bonded exchange.

[f] S-bonded exchange.

[g] Obtained indirectly from substitution reaction studies of L with bidentated ligands.

[h] In $CHCl_3$.

reactions as compared to solvent- and ligand-exchange reactions. A logical question is whether the mechanistic changeovers reported above for particular solvent- and ligand-exchange reactions also occur for ligand substitution processes. A summary of the data available for complex formation reactions of divalent first-row transition-metal elements in Table VI clearly demonstrate that complex formation reactions exhibit the same trend in $\Delta V^{\#}$ as do the corresponding water-exchange reactions, i.e., a mechanistic changeover from I_a to I_d along the series. Complex formation reactions of Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} in DMF also exhibit $\Delta V^{\#}$ values in good agreement with those reported in Table III for DMF exchange on the hexasolvates.[17] Substitution reactions of a series of polyaminocarboxylato complexes of Ru(III) that involve the replacement of a coordinated water or hydroxy ligand are characterized by $\Delta V^{\#}$ values between -4 and -15 cm^3 mol^{-1},[18–20] which suggest the operation of I_a and A mechanisms. In general complex formation reactions of square-planar Pd(II) complexes (i.e., substitution of a solvent molecule by a neutral or anionic nucleophile) exhibit very similar $\Delta V^{\#}$ values as compared to those for water-exchange. Furthermore, $\Delta V^{\#}$ becomes more negative for larger entering ligands[21] and exhibits a fairly good correlation with the overall reaction volume as shown in Fig. 4. In the latter reactions it should be kept in mind that both $\Delta V^{\#}$ and $\Delta \overline{V}$ contain

TABLE VI

$\Delta V^{\#}$ for the interchange of neutral and uninegative ligands on M^{2+} ions in water (Ref. 5).

Ligand[a]	V^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
H_2O	−4.1	−5.4	+3.8	+6.1	+7.2		
NH_3				+4.8	+6.0		
Imidazole					+11.0		
Isoquinoline					+7.4		
pada				+7.9	+7.1		
bpy		−1.2		+5.9	+5.3		
terpy		−3.4	+3.6	+4.1	+5.6		
SCN^-	−5.3						
Glycinate(1−)				+5	+7	+9	+4
Murexide(1−)					+8.7		

[a] pada = pyridine-2-azo-4-dimethylaniline; bpy = 2,2′-bipyridine: terpy = 2,2′:6′,2″-terpyridine.

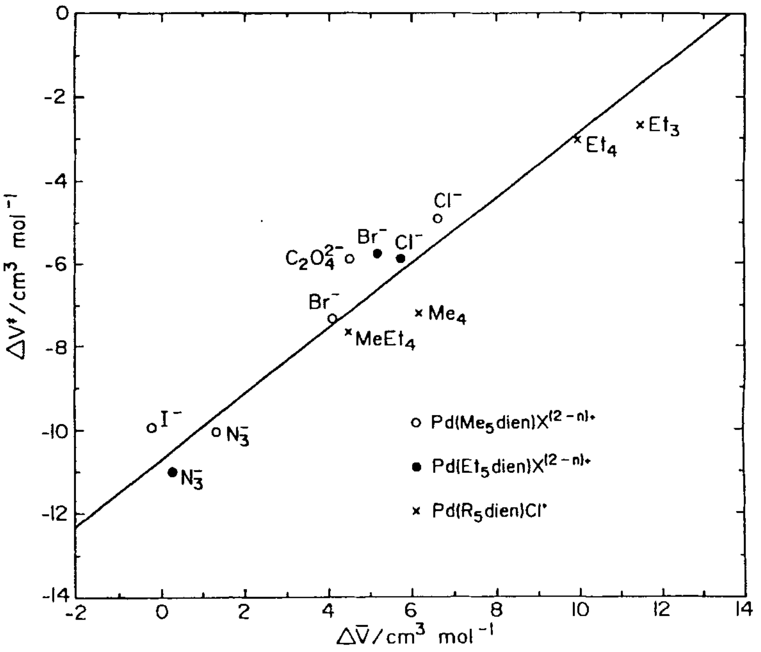


FIGURE 4 Plot of $\Delta V^{\#}$ versus $\Delta\bar{V}$ for a series of anation reactions of the type (Ref. 22):

$$\mathrm{Pd(R_5dien)H_2O^{2+}} + \mathrm{X^{n-}} \rightarrow \mathrm{Pd(R_5dien)X^{(2-n)+}} + \mathrm{H_2O}.$$

contributions from a decrease in electrostriction due to charge neutralization during bond formation with an anionic nucleophile.

Aquation and solvolysis reactions of octahedral and square-planar complexes, i.e., the reverse reaction of complex formation discussed above, also exhibit very characteristic $\Delta V^{\#}$ values. One of the most exciting examples involves the aquation of pentaammine complexes of Co(III) and Cr(III), for which controversial arguments have been reported in the literature for many years.[3,23] A recent study of a series of aquation reactions involving neutral leaving ligands, in order to reduce possible contributions resulting from changes in electrostriction, revealed $\Delta V^{\#}$ values in good agreement with those found for the water-exchange processes (see Table VII). The data strongly support the operation of an I_a mechanism in the case of the Cr(III) complexes compared to an I_d

TABLE VII

Activation parameters and comparative rates for aquation of $M(NH_3)_5L^{3+}$ ions.[24,25]

L	10^5k^a s^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J K^{-1} mol^{-1}	$\Delta V^{\#}$ cm^3 mol^{-1}
		M = Cr(III)		
OH_2	5.2	97.0	0.0	−5.8
$OS(CH_3)_2$	1.95	95.3 ± 0.8	−15 ± 3	−3.2 ± 0.1
$OCHNH_2$	5.1	94.0 ± 1.7	−12 ± 5	−4.8 ± 0.3
$OC(NH_2)_2$	2.0	93.5 ± 1.4	−22 ± 4	−8.2 ± 0.5
$OC(NHCH_3)_2$	1.0	97.5 ± 0.5	−14 ± 2	−3.8 ± 0.2
$OCHN(CH_3)_2$	1.45	93.1 ± 1.8	−25 ± 5	−7.4 ± 0.1
$OC(CH_3)N(CH_3)_2$	1.9	91.9 ± 2.0	−30 ± 6	−6.2 ± 0.4
$OP(OCH_3)_2$	6.0	89.7 ± 0.9	−23 ± 3	−8.7 ± 0.1
		M = Co(III)		
OH_2	0.59	111	+28	+1.2
$OS(CH_3)_2$	1.8	103	+10	+2.0
$OCHNH_2$	0.58	107	+12	+1.1
$OC(NH_2)_2$	5.5	94	−10	+1.3
$OC(NHCH_3)_2$	5.1	102	+17	+1.5
$OCHN(CH_3)_2$	0.16	111	+16	+2.6
$OHCH_3$	6.5	98	+5	+2.2
$OHCH_2CH_3$	8.5	99	+9	+2.9
$OHCH(CH_3)_2$	33.6	98	+16	+3.8
$OC(NH_2)(NHCH_3)$	4.1	98	+2	+0.3
$OCH\cdot(NHCH_3)$	0.25	108	+13	+1.7

[a] Aquation rate at 25°C.

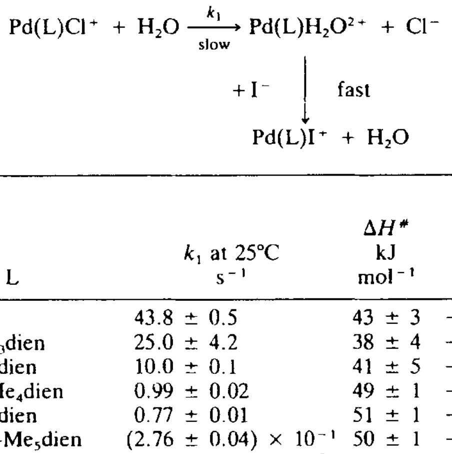
mechanism in the case of Co(III) complexes. A volume profile treatment of the data also supports a mechanistic differentiation.[25] Solvolysis reactions of the type (2)

$$M(NH_3)_5(OSO_2CF_3)^{2+} + \text{solvent} \rightarrow M(NH_3)_5(\text{solvent})^{3+} + CF_3SO_3^- \quad (2)$$

exhibit $\Delta V^{\#}$ values that decrease from −3 to −10 cm^3 mol^{-1} along the series Co(III) > Rh(III) > Cr(III) in MeCN and MeOH as solvents.[26] This trend supports a changeover from I_d to I_a mechanism along the series, if the decrease in volume due to increasing electrostriction (charge creation) is taken into consideration. By way of comparison, typical dissociatively activated solvolysis reactions of pentacyanoiron(II/III) complexes exhibit $\Delta V^{\#}$ values ranging from $+20$ to $+27\ \mathrm{cm^3\ mol^{-1}}$, which support a limiting D mechanism.[27,28] On the other hand, solvolysis reactions of a diethylenetriamine(dien) and substituted dien complexes of Pd(II) exhibit significantly negative $\Delta V^{\#}$ values (Table VIII) in agreement with an associative mechanism. The data in Table VIII nicely demonstrate that the introduction of steric hindrance (Me and Et substituents on the dien ligand) decreases the solvolysis rate constant by up to six orders of magnitude, but does not affect the nature of the substitution process since both $\Delta S^{\#}$ and $\Delta V^{\#}$ remain strongly negative. The nature of the leaving group does affect the value of $\Delta V^{\#}$ and may indicate the operation of an I_a mechanism.[30] Nevertheless, very significant is our finding that steric hindrance alone cannot change the nature of the substitution mechanism for square planar complexes (compare data in Table V).[21,31] With the available $\Delta V^{\#}$ for both complex formation and reverse aquation

TABLE VIII

Kinetic parameters for the reaction (Ref. 29)



$$\begin{tikzcd} \mathrm{Pd(L)Cl^+ + H_2O} \arrow[r, "k_1", "\mathrm{slow}"'] & \mathrm{Pd(L)H_2O^{2+} + Cl^-} \arrow[d, "\mathrm{fast}", "+\mathrm{I^-}"'] \\ & \mathrm{Pd(L)I^+ + H_2O} \end{tikzcd}$$

L	k_1 at 25°C $\mathrm{s^{-1}}$	$\Delta H^{\#}$ kJ $\mathrm{mol^{-1}}$	$\Delta S^{\#}$ J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$	$\Delta V^{\#}$ at 25°C $\mathrm{cm^3}$ $\mathrm{mol^{-1}}$
dien	43.8 ± 0.5	43 ± 3	−69 ± 12	−10.0 ± 0.6
1,4,7-$\mathrm{Me_3}$dien	25.0 ± 4.2	38 ± 4	−87 ± 15	−9.2 ± 0.6
1,4,7-$\mathrm{Et_3}$dien	10.0 ± 0.1	41 ± 5	−86 ± 18	−10.8 ± 1.0
1,1,7,7-$\mathrm{Me_4}$dien	0.99 ± 0.02	49 ± 1	−79 ± 3	−13.4 ± 1.9
1,1,4-$\mathrm{Et_3}$dien	0.77 ± 0.01	51 ± 1	−76 ± 3	−14.5 ± 1.2
1,1,4,7,7-$\mathrm{Me_5}$dien	$(2.76 \pm 0.04) \times 10^{-1}$	50 ± 1	−88 ± 3	−10.9 ± 0.3
1,1,7,7-$\mathrm{Et_4}$dien	$(2.1 \pm 0.4) \times 10^{-3}$	69 ± 2	−67 ± 8	−14.9 ± 0.2
4-Me-1,1,7,7-$\mathrm{Et_4}$dien	$(6.8 \pm 0.1) \times 10^{-4}$	66 ± 7	−84 ± 25	−14.3 ± 0.6
1,1,4,7,7-$\mathrm{Et_5}$dien	$(6.7 \pm 0.1) \times 10^{-4}$	59 ± 3	−106 ± 9	−12.8 ± 0.8

reactions of Pd(II) complexes, it is possible to construct relative reaction volume profiles for the overall process. A few examples are given in Fig. 5, from which it follows that the transition state has a significantly lower partial molar volume than either the reactant or product species, demonstrating the associative character of the substitution process even when we take possible electrostriction effects into account.

Another type of ligand substitution reaction that exhibited an interesting and remarkable pressure dependence is the base-catalyzed aquation, i.e., base hydrolysis, reactions of pentaamminecobalt(III) complexes.[3] These are generally accepted to proceed according to a S_N1CB mechanism as outlined in (3),

$$\begin{aligned} &\mathrm{Co(L)_5X^{(3-n)+} + OH^- \overset{K_1}{\rightleftharpoons} Co(L)_4(L{-}H^+)X^{(2-n)+} + H_2O,} \\ &\mathrm{Co(L)_4(L{-}H^+)X^{(2-n)+} \xrightarrow{k_2} Co(L)_4(L{-}H^+)^{2+} + X^{n-},} \\ &\mathrm{Co(L)_4(L{-}H^+)^{2+} + H_2O \xrightarrow{fast} Co(L)_5OH^{2+}} \qquad (3) \end{aligned}$$

where the dissociation of the conjugate base species $\mathrm{Co(L)_4(L{-}H^+)X^{(2-n)+}}$ (L = amine, $\mathrm{L{-}H^+}$ = deprotonated amine) is the rate-determining step. The volume profile expected for such a reaction scheme is shown in Fig. 6, where the volume of activation for the observed second-order rate constant (k_2K_1) is expressed as $\Delta V^{\#} = \Delta \bar{V}(K_1) + \Delta V^{\#}(k_2)$. Both these quantities are expected to depend strongly on the nature of the leaving group (especially its charge), since an increase in electrostriction will occur when X is anionic. At present, the $\Delta V^{\#}$ data available for 30 different complexes vary between +19 and +43 $\mathrm{cm^3\ mol^{-1}}$, and exhibit a strong dependence on the nature of the leaving group.[32–34] For 23 of these systems the $\Delta V^{\#}$ data could be correlated with the overall $\Delta \bar{V}_{BH}$ value which was determined dilatometrically. All volume quantities exhibit a strong dependence on ΔZ^2 $(=(Z-1)^2 - Z^2 = 1 - 2Z)$, where Z is the charge on the complex undergoing base hydrolysis (see Fig. 7). The contribution of $\Delta \bar{V}(K_1)$ towards $\Delta V^{\#}$ was estimated[34] to be between 17 and 27 $\mathrm{cm^3\ mol^{-1}}$, from which it follows that $\Delta V^{\#}(k_2)$ is a positive quantity under all conditions. All the observed volume data are in good agreement with that expected on the basis of the suggested mechanism. Very re-

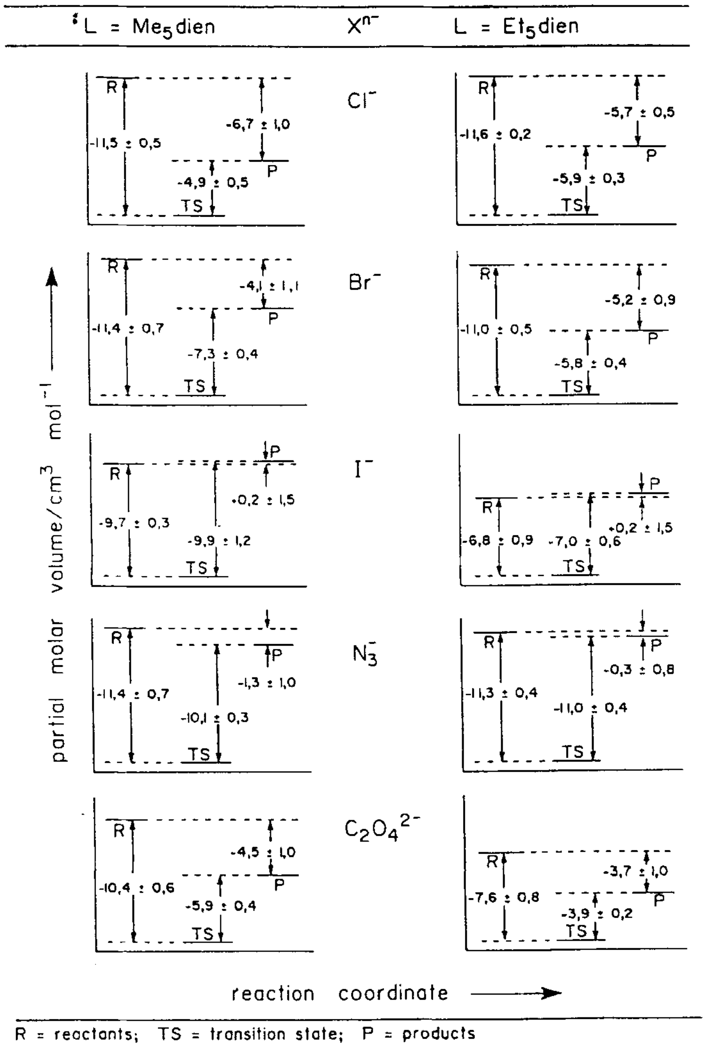


FIGURE 5 Volumes profiles for the reaction (Ref. 22):

$$Pd(L)X^{(2-n)+} + H_2O \rightleftharpoons Pd(L)H_2O^{2+} + X^{n-}.$$

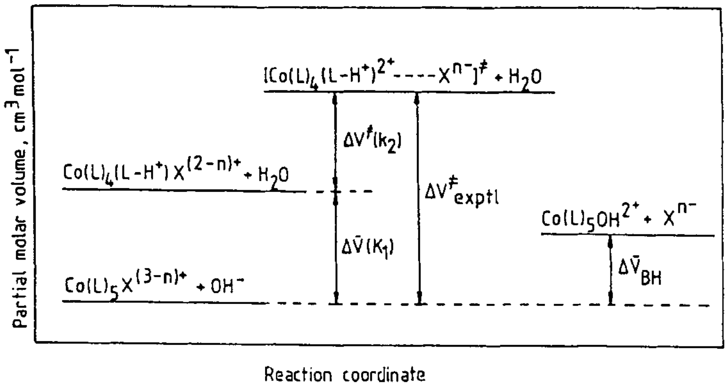


FIGURE 6 Volume profile for the base hydrolysis mechanism outlined in Eq. (3) (from Ref. 34).

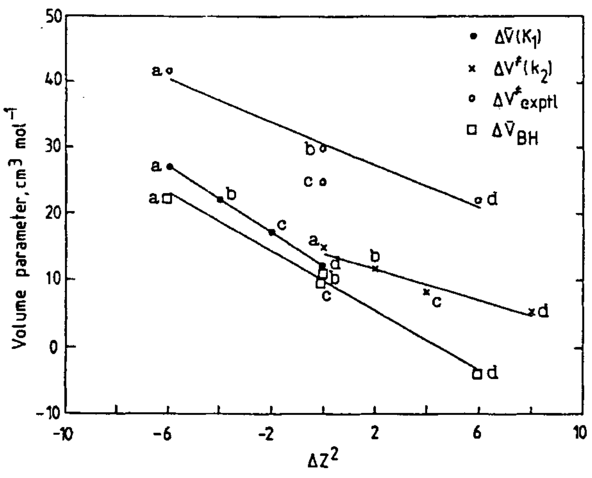


FIGURE 7 Plot of volume parameter versus ΔZ^2. The letters a, b, and c refer to averaged data for 3+, 2+, and 1+ complexes with neutral (a) or 1− leaving groups (b, c), whereas d refers to a 1+ complex with a 2− leaving group (from Ref. 34).

cently the pressure dependence of the base hydrolysis of $\mathrm{Co(tmen)}_3^{3+}$ (tmen = 2,3-diamino-2,3-dimethylbutane) was measured and gave a $\Delta V^{\#}$ of +58 cm^3 mol^{-1}. This large value is ascribed to conjugate base formation and ring-opening of the bulky tmen ligand. A consequence of this large $\Delta V^{\#}$ is that the hydrolysis rate constant decreases by an order of magnitude for a pressure increase of 100 MPa.

In a recent study,[36,37] $\Delta V^{\#}$ for the base hydrolysis of a series of Cr(III) complexes was measured. The observed $\Delta V^{\#}$ values are on the average between 10 and 16 $cm^3\ mol^{-1}$ smaller than the corresponding values for the Co(III) complexes. It was suggested that the conjugate base species in the case of the Cr(III) complexes may undergo an interchange type of substitution process, i.e., significantly more associative than for Co(III) and in agreement with the aquation data discussed before.

Substitution reactions of a number of organometallic complexes and clusters have also been investigated using high pressure kinetic techniques. CO site exchange in $Fe(CO)_2$ (1,3-cyclooctadiene) (PPh_3) was followed by ^1H NMR and showed essentially no pressure dependence.[38] In contrast, CO site exchange on $Fe(CO)_2\{2,3\text{-}\eta\text{:O-}\sigma\text{-}(7,7)\text{-dimethoxybicyclo}(2.2.1)\text{hept-2-ene})\}(PPh_3)$ was found to have a significant positive $\Delta V^{\#}$ so that a dissociative process is operative. Mechanistic uncertainties regarding chelate-ring replacement reactions of $M(CO)_4(\overset{\frown}{S\ S})$ complexes resulting from large differences in values for $\Delta S^{\#}$ were solved with the help of the $\Delta V^{\#}$ data[39] summarized in Table IX for a series of different complexes. The data support a dissociative reaction for all the Cr complexes and an associative reaction for the DTH and dto complexes of Mo. However, on increasing the steric hindrance on the $\overset{\frown}{S\ S}$ ligand, associative attack at the Mo center is hindered and an I_d mechanism seems to be operative in the case of the BTE complex. The data demonstrate the fine tuning of the mechanism by the size of both the central metal and the coordinated ligands. Replacement of coordinated CO by $P(OMe)_3$ on complexes of the type $M(CO)_4$phen is characterized by a $\Delta V^{\#}$ of $+13.8\ cm^3\ mol^{-1}$ for M = Cr compared to $-21\ cm^3\ mol^{-1}$ for M = Mo in 1,2-dichloroethane.[40] These values once again demonstrate the changeover from dissociative to associative in going from Cr to Mo complexes. A volume profile for the Cr system is presented in Fig. 8, which clearly demonstrates the significantly higher partial molar volume of the transition state compared to either the reactant or product states. The overall reaction volume calculated from the difference in $\Delta V_f^{\#}$ and $\Delta V_r^{\#}$ is in close agreement with that obtained from

TABLE IX

Activation parameters and volumes of activation for ligand-displacement reactions of $(S_2)M(CO)_4$ complexes (Ref. 39).

S_2[a]	M	Solvent[a]	L	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}	$\Delta V^{\neq}$ cm^3 mol^{-1}
DTH	Cr	DCE	$P(OMe)_3$	103 ± 1	$+20 \pm 3$	$+10.1 \pm 0.8$
		CB		97 ± 5	0 ± 17	$+8.8 \pm 0.4$
		DCE	$P(OPh)_3$	103 ± 1	$+8 \pm 13$	$+9.3 \pm 0.5$
			$P(O\text{-}i\text{-}Pr)_3$	99 ± 2	0 ± 8	$+10.4 \pm 0.4$
	Mo	DCE	$P(OMe)_3$	71 ± 1	-57 ± 3	-11.3 ± 0.5
			$P(O\text{-}i\text{-}Pr)_3$	79 ± 1	-54 ± 4	-10.2 ± 0.8
			$P(OPh)_3$	68 ± 2	-83 ± 6	-9.3 ± 0.4
dto	Cr	DCE	$P(OEt)_3$	124 ± 6	$+76 \pm 18$	$+14.7 \pm 0.7$
	Mo	CB	$P(O\text{-}i\text{-}Pr)_3$	72 ± 2	-69 ± 7	-9.4 ± 0.2
BTE	Cr	DCE	$P(OEt)_3$	92 ± 6	-8 ± 19	$+14.0 \pm 0.6$
	Mo		$P(O\text{-}i\text{-}Pr)_3$	87 ± 1	-31 ± 2	$+3.9 \pm 0.3$

[a] Abbreviations: DTH—2,5-dithiahexane; dto—3,6-dithiaoctane; BTE—cis-2,2,7,7-tetramethyl-3,6-dithiaoct-4-ene; DCE—1,2-dichloroethane; CB—chlorobenzene.

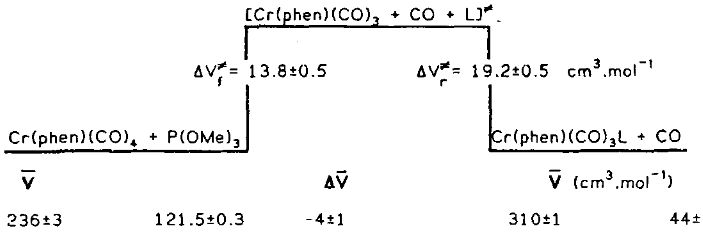


FIGURE 8 Volume profile for the reaction (Ref. 40):

$Cr(phen)(CO)_4 + P(OMe)_3 \rightleftharpoons Cr(phen)(CO)_3(P(OMe)_3) + CO.$

the partial molar volumes of the reactant and product species. Large positive volumes of activation were reported for CO dissociation from Mn(biacetylbis(phenylimine)) $(CO)_3^+$ $(+20.6 \pm 0.4)$,[41] Mn(1,4,7-trithiacyclononane) $(CO)_3^+$ $(+20.6 \pm 2.6)$,[42] $HRu_3(CO)_{11}^-$ $(+21.2 \pm 1.4)$, $Ru_3(CO)_{11}(CO_2CH_3)^-$ $(+16 \pm 2)$ and $Ru_3(CO)_{10}(P(OCH_3)_3)(CO_2CH_3)^-$ $(+24 \pm 2$ cm^3 $mol^{-1})$.[43]

The interest in the mechanistic behaviour of solvento metal carbonyl complexes led to a series of high pressure studies involving the replacement of coordinated solvent molecules. In most cases such species are short-lived and can only be produced via flash-photolysis (see further discussion). In the case of THF as solvent, complexes of the type $M(CO)_5THF$ are stable and can be prepared in solution. A systematic variation of M and the entering ligand resulted in the data in Table X, from which a gradual changeover to a more associative mechanism from Cr to W can be concluded (it must be kept in mind that the overall second-order rate constant is a composite function of at least three individual rate constants that will all exhibit their own characteristic pressure dependences).[44]

b. Addition, Insertion and Elimination Reactions

In general, bond formation processes are characterized by negative volumes of activation, whereas bond breakage processes are characterized by positive values.[3] It is therefore not surprising that oxidative addition reactions are characterized by significantly negative volumes of activation, partially due to bond formation and partially due to charge creation in the transition state. For instance $\Delta V^{\#}$ for the oxidative addition of O_2 to $Ir(cod)phen^+$ and Ir(cod)(phen)I has values of -31 ± 2 and -44 ± 2 cm^3 mol^{-1}, respectively.[45] These values usually depend on the nature of the solvent since the latter controls the extent of changes in electrostriction during such reactions.[46,47] In a similar way, typical cyclo-addition reactions, for instance $Fe(CO)_3HTE$ (HTE = heptatrienone) with tetracyanoethane, are characterized by substantially negative vol-

TABLE X

Summary of the rate and activation parameters for the reaction (Ref. 44):

$$M(CO)_5THF + L \xrightarrow{k} M(CO)_5L + THF.$$

M	Ligand	k(298 K) M^{-1} sec^{-1}	$\Delta G^{\#}_{298}$ kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J mol^{-1} K^{-1}	$\Delta V^{\#}$ cm^3 mol^{-1}
Cr	piperidine	1.53 ± 0.02	72 ± 4	45 ± 2	−90 ± 8	−2.2 ± 0.6
	$P(C_6H_5)_3$	0.36 ± 0.03	76 ± 4	78 ± 2	+8 ± 8	−1.9 ± 1.0
	$P(OC_2H_5)_3$	0.37 ± 0.02	76 ± 2	53 ± 1	−74 ± 2	−3.6 ± 0.7
Mo	piperidine	15.2 ± 0.6	66 ± 4	60 ± 2	−21 ± 8	−3.6 ± 1.2
	$P(C_6H_5)_3$	2.5 ± 0.1	71 ± 8	65 ± 4	−17 ± 14	−8.3 ± 1.0
	$P(OC_2H_5)_3$	1.73 ± 0.03	72 ± 4	55 ± 2	−55 ± 8	−5.8 ± 0.9
W	piperidine	0.75 ± 0.05	74 ± 6	38 ± 6	−122 ± 2	−4.4 ± 0.5
	$P(C_6H_5)_3$	0.071 ± 0.003	80 ± 7	50 ± 3	−100 ± 11	−12.2 ± 0.4
	$P(OC_2H_5)_3$	0.31 ± 0.01	76 ± 6	49 ± 3	−89 ± 3	−14.9 ± 1.0

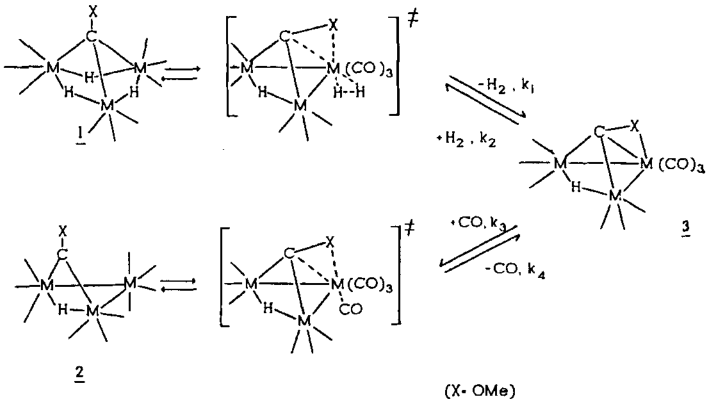
umes of activation, viz. between -29 and $-33\ cm^3\ mol^{-1}$ depending on the solvent.[48]

Insertion reactions into the metal–carbene bond should also accelerate with increasing pressure, i.e., exhibit negative $\Delta V^{\#}$ values. In a recent study[49] the insertion of (phenylmethoxy)pentacarbonyl chromium and tungsten with dipropylcyanamide and 1-diethylamino-1-propyne exhibited significantly negative $\Delta V^{\#}$ values of ca. $-20\ cm^3\ mol^{-1}$. These are to our knowledge the first $\Delta V^{\#}$ data available for such insertion processes and demonstrate the importance of bond formation.

Elimination reactions in general exhibit the opposite pressure effect,[3] viz. a decrease in rate constant with increasing pressure, i.e., a positive $\Delta V^{\#}$ with values as high as $+26\ cm^3\ mol^{-1}$.[50] In a recent study it was found that the reductive elimination of hydrogen from $H_3Ru_3(\mu_3\text{-COMe})\ (CO)_9$ is characterized by a volume of activation of $+20 \pm 2\ cm^3\ mol^{-1}$, whereas the reverse hydrogenation of $HRu_3(\mu\text{-COMe})(CO)_{10}$ is accompanied by a $\Delta V^{\#}$ of $+9.6 \pm 0.6\ cm^3\ mol^{-1}$.[51] These data are interpreted in terms of the overall reaction mechanism outlined in Scheme I.

c. Electron-Transfer Reactions

The effect of pressure on a series of typical outer-sphere electron-transfer reactions has been studied in recent years. These reactions



SCHEME I

exhibit characteristic $\Delta V^{\#}$ values as demonstrated by the following examples ($\Delta V^{\#}$ is quoted in brackets, $cm^3\ mol^{-1}$): MnO_4^-/MnO_4^{2-} (-23 in water)[52]; $Ru(hfac)_3^-$/$Ru(hfac)_3$ (between -5.5 and -8.1 for different organic solvents)[53]; $Fe(phen)_3^{2+}$/$Fe(phen)_3^{3+}$ (-2.2 for D_2O and -5.9 for CD_3CN)[54]; $Co(en)_3^{2+}$/$Co(en)_3^{3+}$ (-20 in water)[55]; $Co(terpy)_2^{2+}$/$Co(bipy)_3^{3+}$ (-9.4 in water)[56]; $Cu(Me_2phen)_2^{+/2+}$ (-3.4 in CD_3CN and -7.4 in $(CD_3)_2CO$).[57] Theoretical calculations based on the Marcus–Hush theory were performed in all cases in an effort to account for the observed $\Delta V^{\#}$ values. These revealed information on the nature of the transition state for the electron-transfer process in terms of its adiabatic or non-adiabatic character, and in general showed a good agreement with the experimental values. In many of the quoted examples there is no net chemical reaction and no net change in charge. The negative volumes of activation are governed by charge creation (i.e., increasing electrostriction) during the electron-transfer process.

In another series of studies the effect of pressure on outersphere electron-transfer reactions between complexes of the type $Co(NH_3)_4(NH_2R)X^{(3-n)+}$ and $Fe(CN)_6^{4-}$ was investigated for the rate-determining electron-transfer reaction within the precursor ion-pair intermediate. The reported $\Delta V^{\#}$ values are $+26.5$ (R = H, X^{n-} = H_2O)[58]; $+29.8$ (R = H, X^{n-} = py)[58]; $+34.4$ (R = H, X^{n-} = DMSO)[58]; $+18.8$ (R = H, X^{n-} = N_3^-)[59]; $+25.9$ (R = H, X^{n-} = Cl^-)[59]; $+25.1$ (R = CH_3, X^{n-} = Cl^-)[59]; $+31.3$ (R = *i* − C_4H_9, X^{n-} = Cl^-).[59] Theoretical calculations indicate that the transition state lies approximately halfway between the reactant and product states on a volume basis along the reaction coordinate. These reactions are accompanied by a substantial decrease in electrostriction due to charge neutralization ($Co^{III} \rightarrow Co^{II}$ and $Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-}$), such that the observed $\Delta V^{\#}$ can largely be accounted for in this way.

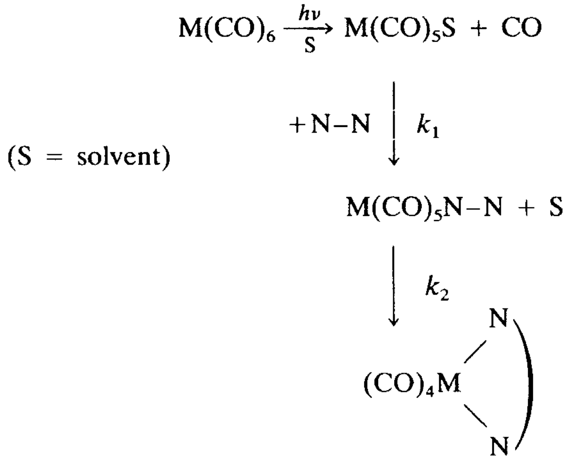
A number of inner-sphere electron-transfer reactions have also been studied using high pressure kinetic techniques,[3,60] but the available data are not so extensive as to allow a detailed analysis similar to that for outer-sphere electron-transfer processes. Nevertheless, the pressure effects are in some cases very significant and result in large activation volumes. A few typical examples of reported data (in $cm^3\ mol^{-1}$) for intramolecular electron-transfer reactions are: $Co(NH_3)_5OSO_2^+$ (+35)[61]; $(NH_3)_5Co^{III}$ (μ-pyrazine)$Fe^{II}(CN)_5$ (+38, +35)[62,63]; $(NH_3)_4Co^{III}$ (μ-pyrazinecarboxylate)Fe^{II} $(CN)_5$ (+24, +28)[63,64]; $(en)_2Co^{III}$ (μ-pyrazinecarboxylate)Fe^{II} $(CN)_5$ (+27).[63] Again these large volume increases must be partly due to charge neutralization or charge dilution during the electron-transfer process.

One particular technique which has recently been applied to the study of mixed-valence compounds is pressure tuning spectroscopy.[65-70] It is well known that pressure effects on the electronic spectrum of a material can provide valuable information about its electronic structure and its interactions with the medium. In a recent study[71] the effect of pressure on the intervalency transfer band of a very weakly coupled binuclear complex (μ-2,6-dithiaspiro[3.3]heptane)decaamminediruthenium(II/III) in D_2O was investigated. The red shift in the band and a small increase in the oscillator strength with increasing pressure was used to estimate the volume of activation for non-adiabatic electron tunnelling. The reported value of $-7.5 \pm 0.2\ cm^3\ mol^{-1}$ indicates that the electron tunnelling rate constant increases with increasing pressure, which is probably related to an increase in electrostriction during the electron-transfer process.

d. Photo-Induced Substitution Reactions

We have shown above that thermal ligand exchange and substitution reactions exhibit characteristic pressure dependencies that assist the assignment of the underlying reaction mechanism. On the other hand, flash photolysis techniques have in general been adopted with great success to study the substitution behaviour of reactive intermediates in organometallic chemistry. In a series of recent studies these techniques were combined in an effort to obtain more mechanistic information on the displacement of solvent in metal carbonyl complexes. In one of the first studies[72] the volume of activation for the displacement of chlorobenzene by pyridine in cis-(C_6H_5Cl) $(PPh_3)W(CO)_4$ was found to be $+11.3 \pm 0.4\ cm^3\ mol^{-1}$, and for the ring-closure reaction in cis-(C_6H_5Cl) $(PPh_2(CH_2)_4C{=}CH_2)W(CO)_4$ $+10.5 \pm 0.3\ cm^3\ mol^{-1}$. Both these values are indicative of a dissociative desolvation mechanism. In a subsequent study,[73] a value of +12.3 $cm^3\ mol^{-1}$ was reported for the dissociation of benzene from $Cr(CO)_5$ (benzene). By now a series of studies have been completed[74] on the pentacarbonyl complexes of Cr, Mo and W for a series of solvents (n-heptane, fluorobenzene, toluene, benzene) and entering nucleophiles (1-hexene, piperidine, pyridine, 2-picoline). The results enable a careful analysis of the intimate nature of these solvent displacement reactions.

When the attacking nucleophile is a bidentate species, flash photolysis of $M(CO)_6$ in the presence of N–N results in the reaction sequence outlined in (4) for M═Cr, Mo and W.



(4)

Detailed kinetic studies at atmospheric pressure for N–N = 1,10-phenanthroline[75,76] could not resolve the nature of the $M(CO)_5N$–N species in terms of whether it is a six or seven coordinate complex depending on the nature of M. A pressure dependence study of both the solvent displacement (k_1) and ring-closure (k_2) steps[77] clearly indicated a gradual changeover from more dissociative to more associative reactions along the series Cr, Mo, W. For instance $\Delta V^{\#}$ for the ring-closure of $Cr(CO)_5$phen is +6.2 compared to $-8.2\ cm^3\ mol^{-1}$ for $W(CO)_5$phen. Obviously the size of the central metal atom controls the nature of the substitution mechanism. Similar studies on the ring-closure reactions of photo-produced

$M(CO)_5N{-}N$ species for N–N = bipyridine, ethylenediamine and 1,4-diisopropyl-1,4-diazabutadiene[78,79] also reveal this gradual changeover in mechanism. In the case of the sterically less hindered ethylenediamine complex, ring-closure for M = Cr also follows an associative substitution mode ($\Delta V^{\#} = -11.9 \pm 1.5\,\mathrm{cm^3\,mol^{-1}}$). Once again, the obtained $\Delta V^{\#}$ values seem to be a good indicator for the underlying substitution mechanism and further work is in progress.

e. Photochemical and Photophysical Processes

Chemical and physical processes that occur in the electronic excited state of an inorganic or organometallic molecule exhibit characteristic pressure dependences. A number of reviews have described the results available at that stage.[3,80] In the case of photochemical ligand substitution processes the pressure dependence of the observed quantum yield is a composite quantity that reflects the pressure dependence of the photoreaction and that of the photophysical non-radiative and radiative deactivation processes. Thus mechanistic information on such photoreactions can only be obtained if the pressure dependence of the chemical and physical processes are known. For instance it was found that non-radiative deactivation of the lowest excited triplet state of pentaamminerhodium(III) complexes in ligand-field photosubstitution reactions exhibits only a minor pressure dependence, such that the observed pressure dependence of the substitution quantum yield represents that of the photochemical reaction.[80] In this way it was possible to demonstrate that photosubstitution reactions of pentaamminerhodium(III) complexes follow a dissociative mechanism whereas pentaamminechromium(III) complexes follow an associative mechanism.[3]

In more recent work the pressure dependence of some typical photochemical organometallic substitution reactions was investigated.[82] Photosubstitution reactions of the type outlined in (5)

$$M(CO)_6 + L \xrightarrow[313\text{ nm}]{h\nu} M(CO)_5L + CO \qquad (5)$$

(M = Cr, Mo, W; L = piperidine, pyridine, acetonitrile) are all accompanied by significantly positive $\Delta V^{\#}$ values, which support the operation of a dissociative mechanism.[83] Volumes of activation for the photosubstitution of the nitrogen donor ligand by PEt_3 in $W(CO)_5(4\text{-X-py})$ were reported[84] to be +5.7 (X = H), +6.3 (X = NC) and +9.9 (X = acetyl) $cm^3\ mol^{-1}$. The effect of pressure on the luminescence lifetimes of the latter two complexes was found to be negligible, and the observed pressure effects were interpreted in terms of a dissociative mechanism. The larger value found for the acetyl substituted complex was ascribed to the participation of a MLCT to LF state transition prior to the dissociation of the ligand.[84] In a third system it was possible to distinguish between associative charge-transfer and dissociative ligand-field CO photosubstitution in $M(CO)_4(phen)$ (M = Cr, Mo, W) on the basis of the observed pressure dependences.[85,86] For these complexes the photoactivity of the lower lying MLCT states has been a controversial issue in the literature. On the one hand it is assumed that excitation of the MLCT state is followed by thermal back population to the higher energy LF state from which a dissociative photosubstitution reaction occurs.[87] On the other hand it is argued that the MLCT states themselves are photo-active and could undergo associative photosubstitution.[88] The pressure dependence of the quantum yield for the substitution of $W(CO)_4(phen)$ by PEt_3 is presented in Fig. 9 as a function of irradiation wavelength. The corresponding volumes of activation are −12.0 and +8.1 $cm^3\ mol^{-1}$ for irradiation at 546 and 366 nm, respectively, and indicate that the photosubstitution process does follow different mechanisms in the MLCT and LF states. Similar results were found for the corresponding Mo complex, viz. −13.3 and +5.7 $cm^3\ mol^{-1}$, respectively. It was concluded on the basis of these data[86] that the charge-transfer and ligand-field states undergo associative and dissociative ligand substitution reactions, respectively. In the case of the smaller chromium complex, associative ligand substitution in the charge-transfer state does not seem to be possible anymore and the corresponding volume of activation is +2.7 compared to +9.6 $cm^3\ mol^{-1}$ for the ligand-field process. These results nicely underline the value of pressure as a key parameter to distinguish between associative and dissociative photosubstitution mechanisms.

Pulsed-laser photoperturbation techniques have been employed

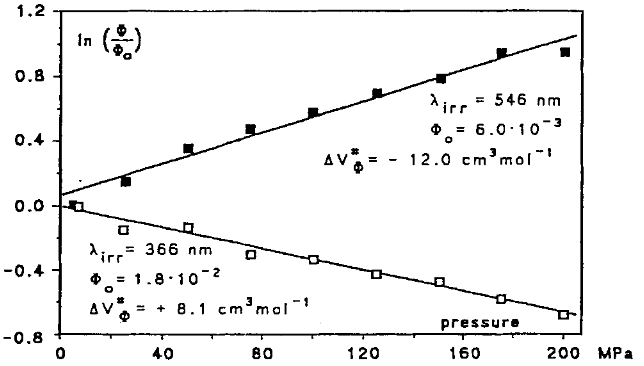


FIGURE 9 Pressure dependence of the quantum yield of the reaction: $W(CO)_4phen + P(C_2H_5)_3 \xrightarrow{h\nu} W(CO)_3[P(C_2H_5)_3]phen + CO$, as a function of irradiation wavelength. T = 298 K, $[P(C_2H_5)_3]$ = 0.135 M (λ_{irr} = 546 nm) and $[P(C_2H_5)_3]$ = 0.0135 M (λ_{irr} = 366 nm) (from Ref. 85).

to study the pressure dependence of low spin–high spin interconversion in a series of Fe(II) complexes in solution.[80,89] The overall reaction volume for the $^1A \rightleftharpoons {}^5T$ spin crossover varies between 4.3 and 16.1 cm^3 mol^{-1} depending on the nature of the ligand and solvent. The activation volume for the forward process is in general significantly positive, whereas the value for the reverse process is almost constant at −6 cm^3 mol^{-1}. It follows that the transition state lies approximately halfway between the low spin and high spin states on a volume basis, and various possible mechanisms have been considered.[89] The data are consistent with a transmission coefficient close to unity.

f. Radiation-Induced Reactions

The mechanisms of inorganic and organometallic free radical reactions have in many cases been studied in detail using pulse-radiolysis techniques, but have not been fully elucidated. This is partly due to the fact that only a limited number of kinetic variables were investigated for such reactions. A series of investigations have therefore been initiated to use pressure as a mechanistic indicator in reactions involving free radicals, induced by pulse radiolysis, that are significantly slower than diffusion controlled.[90-92] The technical difficulties involved to irradiate samples within the high pressure cell were overcome with the aid of a specially designed metal window. The investigated reactions include homolysis, heterolysis, electron transfer, β-elimination and autoxidation, and all exhibit very characteristic pressure dependencies. The corresponding volumes of activation vary between -24 and $+24$ cm^3 mol^{-1}.[90-92] For instance, for the overall reaction in (6)

$$\mathrm{Ni^{II}(cyclam)^{2+}} + \cdot\mathrm{CH_3} \overset{\mathrm{H_2O}}{\rightleftharpoons} \mathrm{Ni^{III}(cyclam)\,(CH_3)H_2O^{2+}} \qquad (6)$$

the reaction volume equals -19.7 cm^3 mol^{-1}, whereas the volumes of activation for the forward and reverse reactions are $+4.7$ and $+24.4$ cm^3 mol^{-1}, respectively.[91] These values indicate that water molecules which are not bound to the divalent nickel complex must move away in order to let the methyl radical reach the central metal cation, and that the two ligands are being bound coherently. In another study $\Delta V^{\#}$ was determined for the key reaction steps in the oxidation of $\mathrm{Cu^{I}(phen)_2^+}$ by molecular oxygen,[92] which proceeds via the formation of $\mathrm{Cu(I){-}O_2}$ as intermediate as outlined in (7).

$$\begin{aligned} \mathrm{Cu(I)} + \mathrm{O_2} &\overset{K}{\rightleftharpoons} \mathrm{Cu(I){-}O_2}, \\ \mathrm{Cu(I){-}O_2} + \mathrm{Cu(I)} &\underset{H^+}{\overset{k}{\rightarrow}} \mathrm{2Cu(II)} + \mathrm{H_2O_2} \end{aligned} \qquad (7)$$

The measured volume of activation of -20 ± 2 cm^3 mol^{-1} for this process can largely be accounted for in terms of the volume collapse during the formation of $\mathrm{Cu(I){-}O_2}$, since $\Delta V^{\#} = \Delta \bar{V}(K) + \Delta V^{\#}(k)$.

Although these are the first $\Delta V^{\#}$ data available for such free radical processes, the results are encouraging and further work is in progress.[93]

g. Reactions Involving Bioinorganic Systems

A number of reviews have been published on the effect of pressure on biophysical and biochemical processes.[2,3,94-96] The work includes studies of the effect of pressure on the structure of proteins, on spin equilibria of iron centers in biological molecules, on ligand binding processes in heme proteins and model systems, and on redox reactions of heme proteins.[3] It is not our objective to give a full account of these activities here, but merely to point out how kinetic studies of such reactions at elevated pressure, performed in our laboratories, have improved our understanding of the involved reaction mechanisms.

The pressure dependence of a number of substitution reactions of aquacobalamin (Vitamin B_{12a}) has been studied and the available activation volumes for the reaction in (8) are summarized in Table XI.

$$B_{12} - H_2O^+ + L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} B_{12} - L^+ + H_2O. \tag{8}$$

TABLE XI

Summary of available $\Delta V^{\#}$ data for the process

$$B_{12}\text{-}H_2O^+ + L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} B_{12}\text{-}L^+ + H_2O.$$

L	$\Delta V^{\#}(k_f)$	$\Delta V^{\#}(k_d)$ $\text{cm}^3\ \text{mol}^{-1}$	$\Delta \bar{V}^{a}$	Ref.
N_3^-	$+6.9 \pm 0.2$			97
$Fe^{II}(CN)_5NO^{2-}$	$+8.9 \pm 0.5$			97
$Fe^{III}(CN)_5H_2O^{2-}$	$+8.2 \pm 0.8$			97
$Fe^{II}(CN)_6^{4-}$	$+16.2 \pm 1.2$			97
$SC(NH_2)_2$	$+3.6 \pm 0.5$	$+6.3 \pm 2.5$	-2.7 ± 3.0	98
$S_2O_3^{2-}$	$+6.0 \pm 0.6$			98
I^-	$+5.5 \pm 0.8$	$+11.5 \pm 1.6$	-5.8 ± 2.3	99
py	$+8.7 \pm 1.2$	$+16.9 \pm 0.8$	-8.2 ± 2.0	100
			-12.0 ± 2.0^{b}	100

[a] $\Delta \bar{V} = \Delta V^{\#}(k_f) - \Delta V^{\#}(k_d)$.
[b] Determined spectrophotometrically.

The results are in agreement with a limiting D mechanism outlined in (9),

$$\begin{aligned} &B_{12} - H_2O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B_{12}^+ + H_2O, \\ &B_{12}^+ + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B_{12} - L^+ \end{aligned} \tag{9}$$

for which $k_f = k_1k_2/k_{-1}$ and $k_d = k_{-2}$. It follows that $\Delta V^{\#}(k_f)$ in Table XI represents $\Delta V^{\#}(k_1) + \Delta V^{\#}(k_2) - \Delta V^{\#}(k_{-1})$ and must therefore depend on the nature of L, especially its charge since changes in electrostriction will affect the value of $\Delta V^{\#}(k_2)$. In the case of L = pyridine, no solvational effects are expected to influence the $\Delta V^{\#}$ data and the reported values mainly represent intrinsic volume changes. A volume profile for the reaction mechanism in (9) is presented in Fig. 10 for L = py.[100] In the latter case it was possible to determine $\Delta V^{\#}(k_1)$ directly from the pressure dependence of the limiting rate constant measured at high concentrations of L, i.e., where k_1 is rate-determining.[100]

In another study the effect of pressure on the formation and deoxygenation kinetics of oxymyoglobin was investigated[101] and a volume profile (Fig. 11) for the overall process was constructed. The results indicate that $Mb-O_2$ bond formation is accompanied

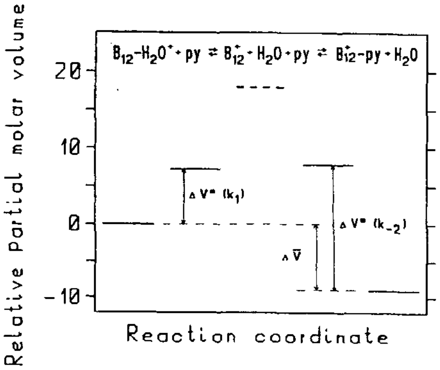


FIGURE 10 Volume profile for the system (Ref. 100):

$B_{12}-H_2O^+ + py \rightleftharpoons B_{12}^+ + H_2O + py \rightleftharpoons B_{12}-py^+ + H_2O$.

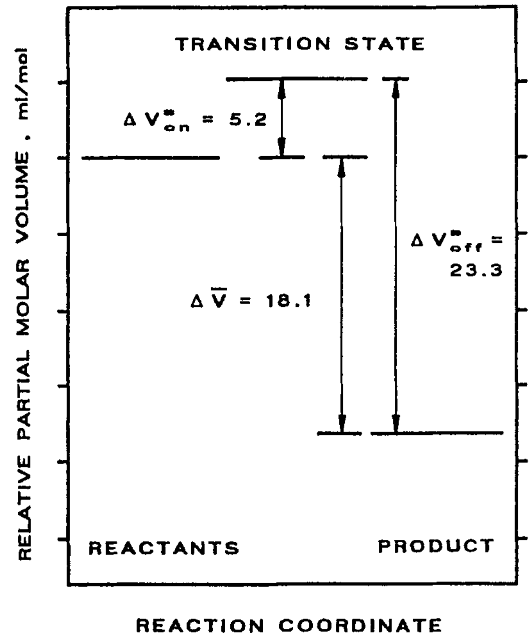


FIGURE 11 Volume profile for the reaction Mb + $O_2 \rightleftharpoons MbO_2$ (from Ref. 101).

by a volume increase presumably due to desolvation as the oxygen molecule finds its way through the protein. In subsequent work[102] the pressure dependence of ligand binding to heme and hemoproteins was studied using picosecond pulsed-laser techniques. A few typical pressure dependences for ligand binding to heme and myoglobin are presented in Figs. 12 and 13. The observed volumes of activation (see Table XII) indicate that in both the protein and models, bond formation is the rate-determining step only for CO, while for O_2, isocyanides and 1-methylimidazole almost no bond formation occurs in the transition state. A 3-state and 4-state mechanism outlined in (10) and (11), respectively, are employed to account for the observed effects.[102]

$$\begin{array}{lll} \mathrm{Hm} - \mathrm{L} \rightleftharpoons & [\mathrm{Hm} \quad \mathrm{L}] \rightleftharpoons & \mathrm{Hm} + \mathrm{L}, \\ \text{bound} & \text{contact} & \text{free ligand} \\ \text{ligand} & \text{pair} & \end{array} \tag{10}$$

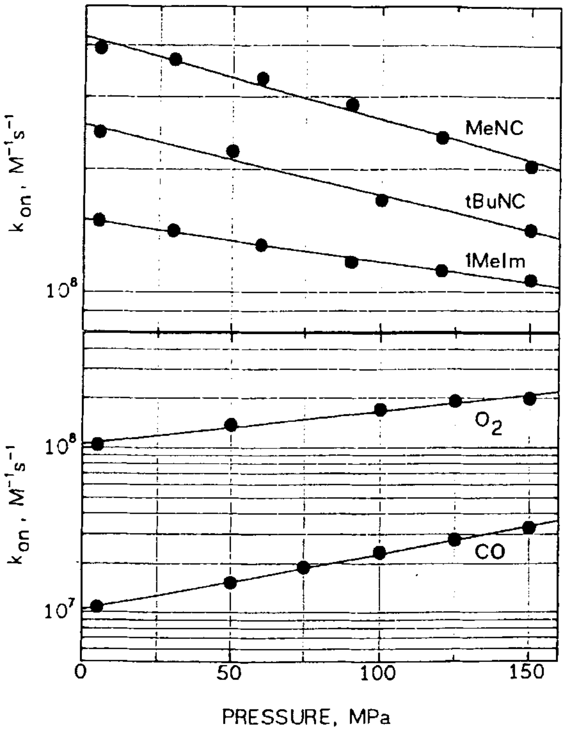


FIGURE 12 Logarithmic plot of k_{on} versus pressure for the reaction (Ref. 102):

$$\text{Heme} + \text{L} \xrightarrow{k_{on}} \text{Heme} - \text{L}.$$

$$\begin{array}{llll} \mathrm{Mb} - \mathrm{L} \rightleftharpoons & [\mathrm{Mb}\quad \mathrm{L}] \rightleftharpoons & [\mathrm{Mb} \,\|\, \mathrm{L}] \rightleftharpoons & \mathrm{Mb} + \mathrm{L} \\ \text{bound} & \text{contact} & \text{protein} & \text{free ligand} \\ \text{ligand} & \text{pair} & \text{separated} & \\ & & \text{pair} & \end{array} \tag{11}$$

The effect of pressure on the escape of CO, O_2 and methyl isocyanide from the heme pocket of Mb was also investigated. The volume increase observed for all ligands during this process is attributed to a "gate-like" conformational change in the protein.

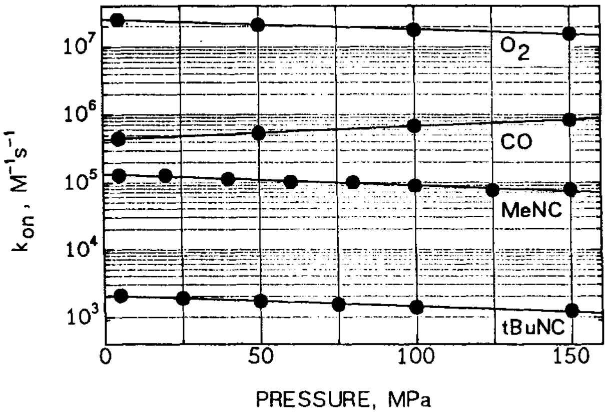


FIGURE 13 Logarithmic plot of k_{on} versus pressure for the reaction (Ref. 102):

$$\text{Mb} + \text{L} \xrightarrow{k_{on}} \text{Mb} - \text{L}.$$

TABLE XII

Volumes of activation for the bimolecular addition of various ligands to five-coordinate Fe(II) model heme complexes and sperm whale myoglobin (Ref. 102).

Reaction	$\Delta V^{\neq}$, $cm^3\ mol^{-1}$
MCPH + CO	−19.3 ± 0.4
MCPH + O_2	−11.3 ± 1.0
(MeNC)PHDME + MeNC	+11.6 ± 0.8
(tBuNC)PHDME + tBuNC	+9.9 ± 1.0
(1MeIm)PHDME + 1MeIm	+10.9 ± 3.1
Mb + CO	−10.0 ± 0.8
Mb + O_2	+5.2 ± 0.5
	+7.8 ± 1.3[a]
Mb + MeNC	+8.8 ± 1.0
Mb + tBuNC	+9.3 ± 0.3

[a] Value reported in Ref. 103.

The results of these studies are a good agreement with those reported by other groups,[104,105] although the exact meaning of an activation volume in such complex systems is still uncertain.[106]

CONCLUSIONS AND FUTURE PERSPECTIVE

The investigated systems reported above have clearly demonstrated that the additional physical parameter pressure has added a decisive dimension to mechanistic studies of inorganic reactions in solution. In this way it is possible to complete the comprehension of chemical kinetics. The investigated systems and types of reactions exhibit very encouraging and systematic pressure dependences, which indicate that we are dealing with a reliable mechanistic indicator. Surely we are not in the position to understand all the observed effects under all conditions especially in the case of reaction types for which only a few data sets are available. On the other hand, $\Delta V^{\#}$ values associated with bond formation and bond breakage processes are understood to a high degree. It is difficult to predict the magnitude of $\Delta V^{\#}$ for limiting substitution mechanisms. However, the sign of $\Delta V^{\#}$ in such processes, especially for low absolute values, has improved the degree of certainty of the suggested mechanism.

In many cases $\Delta V^{\#}$ and $\Delta S^{\#}$ data exhibit similar trends, but exemptions have been reported and possible reasons for the absence of a correlation have been offered.[107] A major advantage of the volume of activation is the fact that it is an activation parameter that can be correlated with a ground state property, viz. the partial molar volumes of the reactant and product species, that can be easily measured experimentally. This has led to the construction of reaction volume profiles as illustrated for a number of examples in this report. Thus the chemical process can be visualized in terms of volume changes along the reaction coordinate.

It is important to emphasize that great care should be taken with the interpretation of $\Delta V^{\#}$ data for chemical processes that involve large changes in electrostriction, as found in many organic systems.[3] The interpretation of such data can usually be supported by a series of measurements in which the charge on the participating species and the solvent polarity is varied systematically.

We realize that the presented interpretations are all based on a simplified version of the transition state theory (TST). This theory definitely has its limitations and restrictions, and various modifications have been suggested (see Ref. 107 for a detailed account). These include the introduction of stochastic and transport models to account for the back-flux over the activated complex barrier in dense media.[108–112] In this sense the TST-language usually used by experimentalists calls for further refinement.[112]

We hope that the inorganic examples selected in this report have attracted the attention of kineticists in such a way that they will seriously consider the application of this technique in future mechanistic studies. High pressure studies is one of the few techniques available to gain insight into the dynamics of excited state species on a molecular level. Application of this technique in the area of photo- and radiation-induced reactions offers many future possibilities. This is also true for the study of complex organometallic and bioinorganic systems. Further extension goes as far as the effect of pressure on living organisms in the deep ocean, viz. bazoenzymology.

The fact that the rate-determining step of a particular process may be accelerated or decelerated by pressure creates the possibility to synthesize selectively a specific reaction product. Some of the presented examples exhibit a large pressure sensitivity, meaning that even the application of moderate pressure could be very helpful in synthetic processes. Furthermore, $\Delta V^{\#}$ data and kinetics should be of predictive value in the optimization of the design of industrial chemical reactions.

Acknowledgments

The authors gratefully acknowledge financial support from the following agencies: RvE—Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Max Buchner Forschungsstiftung, Volkswagen-Stiftung, Nato Scientific Affairs Division; AEM—Swiss National Science Foundation.

References

1. R. van Eldik (Ed.), *Inorganic High Pressure Chemistry: Kinetics and Mechanisms* (Elsevier, Amsterdam, 1986).
2. R. van Eldik and J. Jonas (Eds.), *High Pressure Chemistry and Biochemistry* (Reidel, Dordrecht, 1987).
3. R. van Eldik, T. Asano and W. J. le Noble, Chem. Rev. **89**, 549 (1989).
4. A. E. Merbach, Pure Appl. Chem. **54**, 1479 (1982).
5. A. E. Merbach, Pure Appl. Chem. **59**, 161 (1987).

6. Y. Ducommun and A. E. Merbach, in Ref. 1, p. 69.
7. A. E. Merbach, in Ref. 2, p. 311.
8. M. Kotowski and R. van Eldik, Coord. Chem. Rev. **93**, 19 (1989).
9. J. W. Akitt and A. E. Merbach, in *NMR Basic Principles and Progress*, Volume 24 (Springer-Verlag, Berlin, Heidelberg, 1990), p. 189.
10. M. Spitzer, F. Gartig and R. van Eldik, Rev. Sci. Instrum. **59**, 2092 (1988).
11. S. Wieland and R. van Eldik, Rev. Sci. Instrum. **60**, 955 (1989).
12. C. H. Langford and H. B. Gray, *Ligand Substitution Processes* (W. A. Benjamin, New York, 1965).
13. M. Ishii, S. Funahashi, K. Ishihara and M. Tanaka, Bull. Chem. Soc. Japan (in press).
14. C. Cossy, L. Helm and A. E. Merbach, Helv. Chim. Acta **70**, 1516 (1987).
15. P. Moore and L. Fielding, J. Chem. Soc., Chem. Commun. 49 (1988).
16. M. Ishii, S. Funahashi and M. Tanaka, Chem. Letter 871 (1987).
17. Y. Ducommun, P. J. Nicols and A. E. Merbach, Inorg. Chem. **28**, 2643 (1989).
18. H. C. Bajaj and R. van Eldik, Inorg. Chem. **27**, 4052 (1988).
19. H. C. Bajaj and R. van Eldik, Inorg. Chem. **28**, 1980 (1989).
20. H. C. Bajaj and R. van Eldik, Inorg. Chem. **29**, 2855 (1990).
21. J. Berger, M. Kotowski, R. van Eldik, U. Frey, L. Helm and A. E. Merbach, Inorg. Chem. **28**, 3759 (1989).
22. J. J. Pienaar, M. Kotowski and R. van Eldik, Inorg. Chem. **28**, 373 (1989).
23. G. A. Lawrance and R. van Eldik, J. Chem. Soc., Chem. Commun. 1105 (1987).
24. G. A. Lawrance, Inorg. Chem. **21**, 3687 (1982).
25. N. J. Curtis, G. A. Lawrance and R. van Eldik, Inorg. Chem. **28**, 329 (1989).
26. S. Suvachittanont and R. van Eldik, Inorg. Chem **28**, 3660 (1989).
27. G. Stochel, R. van Eldik, E. Hejmo and Z. Stasicka, Inorg. Chem. **27**, 2767 (1988).
28. G. Stochel and R. van Eldik, Inorg. Chim. Acta **155**, 95 (1989).
29. M. Kotowski and R. van Eldik, in Ref. 1, p. 219.
30. M. Kotowski and R. van Eldik, Inorg. Chem. **25**, 3896 (1986).
31. U. Frey, L. Helm, A. E. Merbach and R. Romeo, J. Am. Chem. Soc. **111**, 8161 (1989).
32. Y. Kitamura, R. van Eldik and H. Kelm, Inorg. Chem. **23**, 2038 (1984).
33. R. van Eldik, Y. Kitamura and C. P. Piriz Mac-Coll, Inorg. Chem. **25**, 4252 (1986).
34. Y. Kitamura, G. A. Lawrance and R. van Eldik, Inorg. Chem. **28**, 333 (1989).
35. H. Diab, P. Hendry, A. Ludi, K. Bal Reddy and R. van Eldik, Inorg. Chim. Acta **175**, 83 (1990).
36. P. Guardado, G. A. Lawrance and R. van Eldik, Inorg. Chem. **28**, 976 (1989).
37. D. A. House, K. Bal Reddy, and R. van Eldik, Inorg. Chim. Acta **186**, 5 (1991).
38. J. Ioset, L. Helm, A. E. Merbach, R. Roulet, F. Grepioni and D. Braga, Helv. Chim. Acta **71**, 1458 (1988).
39. H. H. Awad, C. B. Dobson, G. R. Dobson, J. G. Leipoldt, K. Schneider, R. van Eldik and H. E. Wood, Inorg. Chem. **28**, 1654 (1989).
40. K. J. Schneider and R. van Eldik, Organometallics **9**, 1235 (1990).
41. G. Schmidt, H. Paulus, R. van Eldik and H. Elias, Inorg. Chem. **27**, 3211 (1988).
42. H. Elias, G. Schmidt, H.-J. Küppers, M. Saher, K. Wieghardt, B. Nuber and J. Weiss, Inorg. Chem. **28**, 3021 (1989).

43. D. J. Taube, R. van Eldik and P. C. Ford, Organometallics **6**, 125 (1987).
44. S. Wieland and R. van Eldik, Organometallics **10**, 3110 (1991).
45. D. J. A. de Waal, T. I. A. Gerber, W. J. Louw and R. van Eldik, Inorg. Chem. **21**, 2002 (1982).
46. J. G. Leipoldt, E. C. Steynberg and R. van Eldik, Inorg. Chem. **26**, 3068 (1987).
47. J. A. Venter, J. G. Leipoldt and R. van Eldik, Inorg. Chem. **30**, 2207 (1991).
48. N. Hallinan, P. McArdle, J. Burgess and P. Guardado, J. Organomet. Chem. **333**, 77 (1987).
49. K. J. Schneider, A. Neubrand, R. van Eldik and H. Fischer, Organometallics, in press.
50. M. J. Sisley, W. Rindermann, R. van Eldik and T. W. Swaddle, J. Am. Chem. Soc. **106**, 7432 (1984).
51. J. Anhaus, H. C. Bajaj, R. van Eldik, L. R. Nevinger and J. B. Keister, Organometallics **8**, 2903 (1989).
52. L. Spiccia and T. W. Swaddle, Inorg. Chem. **26**, 2265 (1987).
53. H. Doine and T. W. Swaddle, Inorg. Chem. **27**, 665 (1988).
54. H. Doine and T. W. Swaddle, Can J. Chem. **66**, 2763 (1988).
55. W. H. Jolley, D. R. Stranks and T. W. Swaddle, Inorg. Chem. **29**, 385 (1990).
56. P. Braun and R. van Eldik, J. Chem. Soc., Chem. Commun. 1349 (1985).
57. H. Doine, Y. Yano and T. W. Swaddle, Inorg. Chem. **28**, 2319 (1989).
58. I. Krack and R. van Eldik, Inorg. Chem. **25**, 1743 (1986).
59. I. Krack and R. van Eldik, Inorg. Chem. **29**, 1705 (1990).
60. T. W. Swaddle, Chapter 5 in Ref. 1.
61. R. van Eldik, Inorg. Chem. **22**, 353 (1983).
62. Y. Sasaki, T. Nonomiya, A. Nagasawa, K. Endo and K. Saito, Inorg. Chem. **26**, 2164 (1987).
63. P. Guardado and R. van Eldik, Inorg. Chem. **29**, 3473 (1990).
64. R. Bin-Ali, M. J. Blandamer, J. Burgess, P. Guardado and F. Sanchez, Inorg. Chim. Acta **131**, 59 (1987).
65. H. G. Drickamer, Acc. Chem. Res. **19**, 355 (1986).
66. H. G. Drickamer, Ref. 2, p. 263.
67. M. A. Stroud, H. G. Drickamer, M. H. Zeitlow, H. B. Gray and B. I. Swanson, J. Am. Chem. Soc. **111**, 66 (1989).
68. J. K. McCusker, M. Zvagulis, H. G. Drickamer and D. N. Hendrickson, Inorg. Chem. **28**, 1380 (1989).
69. K. L. Bray and H. G. Drickamer, J. Phys. Chem. **93**, 7604 (1989).
70. A. Lechner and G. Gliemann, J. Am. Chem. Soc. **111**, 7469 (1989).
71. N. A. Lewis, Y. S. Obeng, D. V. Taveras and R. van Eldik, J. Am. Chem. Soc. **111**, 924 (1989).
72. H. H. Awad, G. R. Dobson and R. van Eldik, J. Chem. Soc., Chem. Commun. 1838 (1987).
73. S. Zhang, G. R. Dobson, H. C. Bajaj, V. Zang and R. van Eldik, Inorg. Chem. **29**, 3477 (1990).
74. S. Zhang, V. Zang, H. C. Bajaj, G. R. Dobson and R. van Eldik, J. Organomet. Chem. **397**, 279 (1990).
75. S. Oishi, Organometallics **7**, 1237 (1988).
76. K. Kalyanasundaram, J. Phys. Chem. **92**, 2219 (1988).
77. S. Zhang, V. Zang, G. R. Dobson and R. van Eldik, Inorg. Chem. **30**, 355 (1991).
78. K. Bal Reddy and R. van Eldik, R. Inorg. Chim. Acta **169**, 13 (1990).
79. K. Bal Reddy and R. van Eldik, Organometallics **9**, 1418 (1990).

80. P. C. Ford, Ref. 1 Chapter 6.
81. R. van Eldik, Ref. 2, p. 357.
82. S. Wieland and R. van Eldik, Coord. Chem. Rev. **97**, 155 (1990).
83. S. Wieland and R. van Eldik, J. Phys. Chem. **94**, 5865 (1990).
84. S. Wieland, R. van Eldik, D. R. Crane and P. C. Ford, Inorg. Chem. **28**, 3663 (1989).
85. S. Wieland and R. van Eldik, J. Chem. Soc., Chem. Commun. 367 (1989).
86. S. Wieland, K. Bal Reddy and R. van Eldik, Organometallics **9**, 1802 (1990).
87. D. M. Manuta and A. J. Lees, Inorg. Chem. **25**, 1354 (1986).
88. H. K. van Dijk, P. C. Servaas, D. J. Stufkens and A. Oskam, Inorg. Chim. Acta **104**, 179 (1985).
89. J. McGarvey, I. Lawthers, K. Heremans and H. Toftlund, Inorg. Chem. **29**, 252 (1990).
90. H. Cohen, R. van Eldik, M. Masarwa and D. Meyerstein, Inorg. Chim. Acta **177**, 31 (1990).
91. R. van Eldik, H. Cohen, A. Meshulam and D. Meyerstein, Inorg. Chem. **29**, 4156 (1990).
92. S. Goldstein, G. Czapski, R. van Eldik, H. Cohen and D. Meyerstein, J. Phys. Chem. **95**, 1282 (1991).
93. D. Meyerstein, H. Cohen and R. van Eldik, unpublished results.
94. K. Heremans, Ref. 1, Chapter 7; Ref. 2, p. 339.
95. P. T. T. Wong, Ref. 2, p. 381.
96. G. Weber, Ref. 2, p. 401.
97. G. Stochel, R. van Eldik, H. Kunkely and A. Vogler, Inorg. Chem. **28**, 4314 (1989).
98. A. M. van Herk, Ph.D. Thesis, Free University of Amsterdam (1986).
99. B. B. Hassinoff, Can. J. Chem. **52**, 910 (1974).
100. G. Stochel and R. van Eldik, Inorg. Chem. **29**, 2075 (1990).
101. H.-D. Projahn, C. Dreher and R. van Eldik, J. Am. Chem. Soc. **112**, 17 (1990).
102. D. J. Taube, H.-D. Projahn, R. van Eldik, D. Magde and T. G. Traylor, J. Am. Chem. Soc. **112**, 6880 (1990).
103. B. B. Hassinoff, Biochemistry **13**, 311 (1974).
104. R. G. Alden, J. D. Satterlee, J. Mintorovitch, I. Constantinidis, M. R. Ondrias and B. I. Swanson, J. Biol. Chem. **264**, 1933 (1989).
105. S. Adachi and I. Morishima, J. Biol. Chem. **264**, 18896 (1989).
106. H. Frauenfelder, N. A. Alberding, A. Ansari, D. Braunstein, B. R. Cowen, M. K. Hong, I. E. T. Iben, J. B. Johnson, S. Luck, M. C. Marden, J. R. Mourant, P. Ormos, L. Reinisch, R. Scholl, A. Schulte, E. Shyamsunder, L. B. Sorrensen, P. J. Steinbach, A. Xie, R. D. Young and K. T. Yue, J. Phys. Chem. **94**, 1024 (1990).
107. R. van Eldik, Ref. 1, Chapter 8.
108. J. Schroeder and J. Troe, Am. Rev. Phys. Chem. **38**, 163 (1987).
109. J. Troe, J. Phys. Chem. **90**, 357 (1986).
110. J. Troe, High Pressure Research **5**, 625 (1990).
111. H. Frauenfelder and P. G. Wolynes, Science **229**, 337 (1985).
112. J. Jonas, Acc. Chem. Res. **17**, 74 (1984).