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Pressure as a kinetic parameter in mechanistic studies of chemical reactions induced by flash photolysis and pulse radiolysis

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Abstract

A detailed outline is given of how pressure can be used as a mechanistic indicator in kinetic studies of chemical reactions in solution that are induced by flash photolysis and pulse radiolysis. These techniques have mainly been applied to the study of organometallic and bioinorganic reactions including processes such as ligand substitution, binding of small molecules, formation and breakage of metal-carbon bonds, β-elimination and electron transfer. Typical examples are presented and an account of our most recent work in this area is given.

INTRODUCTION

The application of high pressure kinetic techniques in the study of inorganic, organometallic and bioinorganic reaction mechanisms in solution, has received significant attention from numerous groups over the past decade (ref. 1 to 4). Such studies have added a further dimension to mechanistic investigations by introducing pressure as an additional, and in many cases a decisive, parameter for the elucidation of the underlying reaction mechanism. The fundamental principles involved, the determination of activation and reaction volumes, the construction of reaction volume profiles, and the interpretation of the observed volume changes have been treated in detail elsewhere (ref. 1 to 4) . The basic idea is that the volume of activation represents the change in partial molar volume on going from the reactant to the transition state of the process, such that the reaction volume profile can be analyzed in terms of volume changes along the reaction coordinate.

In this contribution we will focus on examples mainly from organometallic and bioinorganic chemistry where the combination of high pressure kinetic and flash-photolysis of pulse-radiolysis techniques has been employed in an effort to improve our understanding of the intimate mechanism of the process. Work performed by our own group has benefitted greatly from intensive collaboration with other groups mentioned in the cited references. In the remainder of this contribution examples for various types of reactions will be presented, followed by a few conclusive remarks.

LIGAND SUBSTITUTION REACTIONS

Ligand substitution reactions of transition metal complexes have been the topic of many mechanistic investigations because of the fundamental importance of such reactions in many chemical and biochemical processes. There are basically three simple pathways along which ligand substitution reactions can occur: the dissociative (D) process with an intermediate of lower coordination number: the associative (A) process with an intermediate of higher

coordination number: the interchange (I) process in which no intermediate is involved and either bond breakage (I_d) or bond formation (I_a) is the dominant process. In thermal substitution reactions such bond formation/bond breakage processes are characterized by specific intrinsic volume changes and associated pressure dependencies (ref. 1 to 3). Is this also the case for photo- and radiation-induced processes?

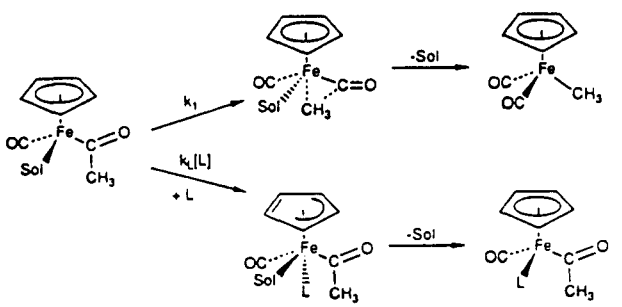
Earlier work has shown that chemical and physical processes that occur in the electronic excited state of an inorganic or organometallic molecule exhibit characteristic pressure dependencies (ref. 5 and 6). From the effect of pressure on the observed quantum yield for a photochemical ligand substitution process and the pressure dependence of the excited state lifetime, it is possible to elucidate the substitution mechanism in the excited state of for instance Rh(III) and Cr(III) amine complexes (ref. 1). Photosubstitution reactions of hexacarbonyl metal complexes outlined in (1), are all accompanied by significantly positive $\Delta V^{\#}$ values, which support the

$$M(CO)_6 + L \xrightarrow[313\ nm]{h\upsilon} M(CO)_5L + CO \qquad (1)$$

M = Cr, Mo, W; L = piperidine, pyridine, CH_3CN

operation of a dissociative mechanism (ref. 7). Contradictions in the literature concerning the photosubstitution mechanism of CO in $M(CO)_4$phen (M = Cr, Mo, W) could be resolved by studying the pressure dependence of the quantum yield as a function of irradiation wavelength (ref. 8).The results demonstrated that for the Mo and W complexes MLCT and LF photosubstitution occurred according to associative and dissociative mechanisms, respectively, whereas the dissociative reaction path was preferred for both processes in the case of the smaller Cr complex. In a similar way the mechanism of the MLCT photochemistry of $(CO)_5ReMn(CO)_3(\alpha\text{-diimine})$ complexes could be resolved (ref. 9).

Photolysis of $CpFe(CO)_2(COCH_3)$ in the presence of $P(OMe)_3$ in n-heptane leads to competitive decarbonylation and ligand substitution to give $CpFe(CO)_2CH_3$ and $CpFe(CO)(P(OMe)_3)COCH_3$, respectively. Application of pressure changes the relative quantum yields and favours the ligand substitution pathway (ref. 10). This could be interpreted in terms of the competitive reactions of the solvento intermediate shown in (2), in which ligand substitution proceeds via an associative mechanism, whereas methyl migration requires simultaneous solvent dissociation, thus opposite pressure dependencies.



(2)

Flash photolysis techniques have been adopted with great success to study the substitution behaviour of reactive solvento intermediates of the type $M(CO)_5S$ shown in (3). The effect of pressure on such reactions have

$$M(CO)_6 \xrightarrow[S]{h\upsilon} M(CO)_5S + CO \qquad (3)$$

$$M(CO)_5S + L \longrightarrow M(CO)_5L + S$$

TABLE 1. Kinetic data for ring-closure of $Mo(CO)_5L$ complexes

Solvent	L [a]	k at 25 °C s^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J $K^{-1}mol^{-1}$	$\Delta V^{\#}$ cm^3mol^{-1}
Toluene	en	3.0×10^{-5}	72 ± 7	-92 ± 22	-5.4 ± 0.8
Toluene	$dabR_2$	1.1×10^{-3}	78 ± 5	-40 ± 17	-9.5 ± 0.4
Toluene	dpbpy	1.4	69 ± 2	-4 ± 6	+5.4 ± 0.5
Toluene	dmbpy	2.6	65 ± 1	-20 ± 3	-5.6 ± 0.4
Toluene	bpy	3.1	62 ± 1	-26 ± 3	-3.9 ± 0.6
Fluorobenzene	phen	1.1×10^{4}	47 ± 2	-9 ± 7	-2.9 ± 0.2

[a] Abbreviations: en = ethylenediamine, $dabR_2$ = 1,4-diisopropyl-1,4-diazabutadiene, dpbpy = 4,4′-diphenyl-2,2′-bipyridine, dmbpy = 4,4′-dimethyl-2,2′-bipyridine, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline

clearly demonstrated the crucial role played by the size of the metal center M, the bulkiness of L and the binding properties of the solvent S in controlling the nature of the substitution mechanism (ref. 11 and 12). In a similar way, it is also possible to study the displacement of a coordinated solvent molecule via ring-closure of a potential bidentate ligand such as a P-olefin. Ring-closure of $cis\text{-}(CO)_4W(S)(PPh_2(CH_2)_nCH = CH_2)$ (n = 1 to 4, S = chlorobenzene) significantly slows down on increasing pressure and results in $\Delta V^{\#}$ values of +7.7, +5.1, +10.7 and +10.5 cm^3mol^{-1} for n = 1 to 4, respectively (ref. 13). These results indicate that chelate ring-closure for n = 1 and 2 follows an interchange (I_d) mechanism in which the olefin moiety is pre-associated with the metal center followed by rate-determining loss of S. In the case of ring-closure for n = 3 and 4, $\Delta V^{\#}$ reaches the limiting value observed for the dissociation of S and presumably does not involve any significant pre-association. Flash photolysis studies of $Cr(CO)_6$ in pure and mixed solvents enable a detailed insight into the displacement mechanism of different solvents coordinated to $Cr(CO)_5$. The reported pressure dependencies indicate for instance that displacement of fluorobenzene follows a dissociative mechanism, whereas displacement of n-heptane takes place via competitive dissociative and interchange pathways (ref. 14).

When the entering nucleophile is a bidentate ligand, flash photolysis of $M(CO)_6$ results in the reaction sequence outlined in (3), followed by CO displacement during ring-closure of the chelate. The $\Delta V^{\#}$ data reported for such reactions (ref. 15 to 18) indicate that the larger metal centers (Mo and W) tend to ring-close in an associative way, whereas the smaller Cr center must loose CO prior to ring-closure, unless there are no bulky groups on the entering chelate that prevent an associative ring-closure reaction. The series of typical results in Table 1 clearly demonstrate a changeover in mechanism from I_a to I_d with increasing steric hindrance on the bidentate ligand L (ref. 17).

LIGATION REACTIONS

The binding of small molecules such as O_2, CO and NO to ferrous hemes and hemoproteins are of fundamental interest to the transport of such molecules in biological systems. Application of flash-photolysis techniques has suggested that in the case of model hemes the germinate pair [Fe L] exists as a single kinetic intermediate as shown in (4), whereas the germinate pair exists in two configurations in the case of proteins as shown in (5).

Mechanistic information on the various steps could be obtained from a detailed pressure dependence study

$$\text{Fe - L} \rightleftharpoons [\text{Fe} \quad \text{L}] \rightleftharpoons \text{Fe} + \text{L} \qquad (4)$$

$$\underset{\text{contact pair}}{\text{Fe - L} \rightleftharpoons [\text{Fe} \quad \text{L}]} \rightleftharpoons \underset{\text{separated pair}}{[\text{Fe} \parallel \text{L}]} \rightleftharpoons \text{Fe} + \text{L} \qquad (5)$$

of the binding kinetics of small neutral molecules to ferrous hemes and hemoproteins (ref. 19). Typical $\Delta V^{\#}$ data for the addition of neutral ligands to two model heme systems, viz. protoheme dimethyl ester (PHDME) and monochelated protoheme (MCPH), are summarized in Table 2. The correlation between k_{on} and $\Delta V^{\#}$ can be attributed to a change in rate-determining step in (4). For the slower reactions recombination characterized by a negative $\Delta V^{\#}$ value is rate-limiting, whereas for the faster reactions the processes become diffusion controlled in toluene and are slowed down by increasing pressure due to a significant increase in solvent viscosity, for which $\Delta V^{\#}_{vis} = +22$ cm^{3}mol^{-1}.

In a subsequent study (ref. 20), the reaction of CO with MCPH was studied as a function of pressure in a highly viscous medium, viz. 90/10 (v/v) mineral oil/toluene. A typical set of results shown in Figure 1, clearly indicate a changeover in rate-determining step from bond formation to diffusion-controlled on increasing the pressure. The data in the low pressure range correspond to a $\Delta V^{\#}$ value of -9.6 cm^{3}mol^{-1}, as compared to a value of +7.1 cm^{3}mol^{-1} in the high pressure range. These data clearly demonstrate how the different steps in reaction (4) can become rate-limiting as a function of the viscosity of the medium and the applied pressure.

Similar techniques were applied to study the association of sperm whale myoglobin with a series of neutral ligands in water as solvent (ref. 19, 21 and 22). The results in Table 3 demonstrate that only the binding of CO is characterized by a negative $\Delta V^{\#}$ value in line with a bond formation process. The positive $\Delta V^{\#}$ values for the other ligands are ascribed to rate-determining entering of the ligand into the protein, which will be accompanied by significant desolvation and presumably conformational changes on the protein chain. By way of comparison, the effect of pressure on the escape of the ligand from the protein-separated pair resulted in significantly positive $\Delta V^{\#}$ values (ref. 19). The observed data is consistent with the notion of a "gate" that operates on the protein in both directions, and reflects both small conformational changes in the protein and solvation of the exiting ligand.

TABLE 2. $\Delta V^{\#}$ data for the bimolecular addition of various neutral ligands to five-coordinate ferrous model heme complexes in toluene as solvent

Heme complex	L	k_{on}(25 °C) $M^{-1}s^{-1}$	$\Delta V^{\#}$ cm^{3}mol^{-1}
MCPH	CO	1.1×10^7	-19.3 ± 0.4
MCPH	O_2	1.0×10^8	-11.3 ± 1.0
(MeNC)PHDME	MeNC	3.9×10^8	+11.6 ± 0.8
(t-BuNC)PHDME	t-BuNC	2.5×10^8	+9.9 ± 1.0
(1-MeIm)PHDME	1-MeIm	1.5×10^8	+10.9 ± 3.1

TABLE 3. $\Delta V^{\#}$ data for the bimolecular addition of various ligands to deoxymyoglobin in aqueous buffer

L	k_{on} (25 °C) $M^{-1}s^{-1}$	$\Delta V^{\#}$ cm^{3}mol^{-1}
CO	5.2×10^5	-10.0 ± 0.8
O_2	2.5×10^7	+5.2 ± 0.5 [a]
	1.3×10^7	+7.8 ± 1.3
MeNC	1.4×10^5	+8.8 ± 1.0
t-BuNC	2.1×10^3	+9.3 ± 0.3

[a] Data obtained using T-jump technique (ref. 21)

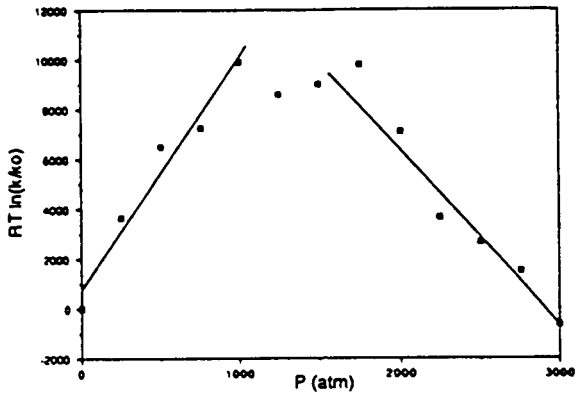


Figure 1. Plot of $RT\ln(k/k_o)$ versus pressure for the reaction of CO with MCPH

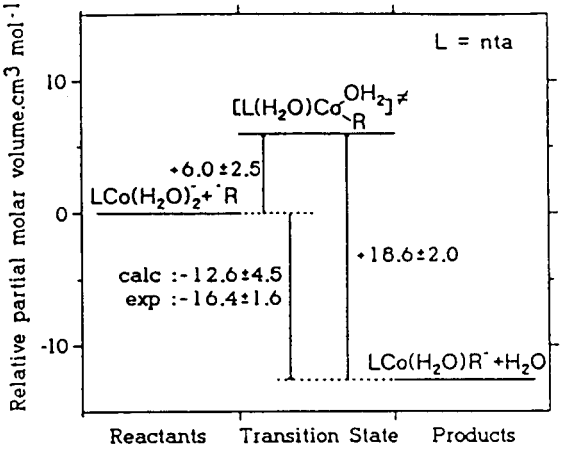


Figure 2. Volume profile for reaction (8)

The large difference in $\Delta V^{\#}$ observed for the binding of O_2 and CO to deoxymyoglobin (Table 3) led to a detailed volume profile analysis of these systems in which high pressure T-jump and stopped-flow techniques were used to study the on and off reactions, respectively (ref. 21 and 22). The observed differences can be accounted for in terms of different rate-determining steps for the on reaction and the nature of the binding of the ligands in the protein pocket.

High pressure pulse-radiolysis experiments were used to demonstrate that the oxidation of $Cu^{I}(phen)_2$, phen = 1,10-phenanthroline, by molecular oxygen proceeds via a Cu^{I}-O_2 transient in which a copper-oxygen bond is formed (ref. 23). This process is characterized by a $\Delta V^{\#}$ value of -22 ± 2 cm^3mol^{-1}, which is close to the reaction volume expected for such a binding process. Depending on the concentration of $Cu^{I}(phen)_2$ present in solution, this transient may either react with another $Cu^{I}(phen)_2$ species or decompose to $Cu^{II}(phen)_2$ and O_2^- as shown in reaction (6).

$$\begin{array}{l} Cu^{I} + O_2 \rightleftharpoons Cu^{I}\text{-}O_2 \quad \begin{array}{l} \nearrow\ 2\ Cu^{II} + O_2^{2-} \\ \searrow\ Cu^{II} + O_2^{-} \xrightarrow{Cu^{I}} Cu^{II} + O_2^{2-} \end{array} \end{array} \qquad (6)$$

FORMATION AND CLEAVAGE OF METAL–CARBON σ BONDS

The mechanisms of free radical reactions can conveniently be studied by using pulse-radiolysis techniques. We developed a special interest in the reaction of alkyl radicals with metal complexes that lead to the formation of metal-carbon σ bonds in aqueous solution. For this purpose a special window was designed for the high pressure cell that allows the penetration of 2 and 5 MeV electrons (ref. 24). The reaction of the methyl radical with the Ni(II) and Co(II) complexes in reactions (7) and (8), is accompanied by reaction volumes of -20 and -16 cm^3mol^{-1}, respectively (ref. 25 and 26). These values indicate that metal-carbon σ bond formation is

$$Ni^{II}(cyclam)^{2+} + \cdot CH_3 + H_2O \rightleftharpoons Ni^{III}(cyclam)(CH_3)(H_2O)^{2+} \qquad (7)$$

$$Co^{II}(nta)(H_2O)_2^- + \cdot CH_3 \rightleftharpoons Co^{III}(nta)(CH_3)(H_2O)^- + H_2O \qquad (8)$$

significantly assisted by pressure, most probably due to the large volume collapse during the formal oxidation of the metal center. Surprisingly, both reactions exhibit small positive volumes of activation for the forward bond formation reactions, indicating that desolvation or partial dissociation of a coordinated solvent molecule must occur prior to metal-carbon bond formation. The corresponding volume profile for reaction (8) is presented in Figure 2 and clearly indicates the significantly higher partial molar volume of the transition state than either the reactant or product states. This is interpreted in terms of an I_d mechanism in which the forward reaction is controlled by solvent exchange on $Co(nta)(H_2O)_2^-$. The large volume collapse following the transition state is ascribed to metal-carbon bond formation which is accompanied by oxidation of Co(II) to Co(III).

A similar result was found for the reaction of aquated Cr(II) with 10 different aliphatic radicals, for which $\Delta V^{\#}$ varied between +3.4 and +6.3 cm^3mol^{-1} with an average value of $+4.3 \pm 1.0$ cm^3mol^{-1} (ref. 27). These data were interpreted as strong evidence for an I_d substitution mechanism for aquated Cr(II), most probably induced by the Jahn-Teller distortion on this ion. Combining these data with that for the reverse homolysis reaction, resulted in the volume profile given in Figure 3, which closely resembles that for the $Co(nta)(H_2O)_2^-$ system in Figure 2. Once again the large volume collapse following the transition state must be due to Cr-R bond formation and $Cr^{II}\text{-}R \rightarrow Cr^{III}\text{-}R^-$. The produced $Cr^{III}\text{-}R^-$ species undergo subsequent homolysis and heterolysis reactions, of which the latter can be catalyzed by the presence of inorganic and organic anions (ref. 28 and 29). In general such $Cr^{III}\text{-}R^-$ complexes are extremely labile, due to the strong trans-labilization effect of the metal-carbon bond, and form unstable complexes with the mentioned anions. Pressure dependence studies provided evidence for a dissociative heterolysis mechanism under influence of the coordinated anions (ref. 28 and 29).

These and more recent studies on the interaction of metal complexes with free radicals, suggest that for non-diffusion-controlled processes, these species can be treated as normal nucleophiles in ligand substitution processes (ref. 30). The produced metal-carbon complexes can in addition to the decomposition reactions mentioned above, also undergo β-elimination reactions that also exhibit characteristic pressure dependencies (ref. 31).

ELECTRON-TRANSFER REACTIONS

The effect of pressure on many inner-sphere and outer-sphere electron-transfer reactions in inorganic and organometallic chemistry has been studied using conventional and fast (stopped-flow and NMR) kinetic techniques (ref. 1, 2, 32 to 36). In many cases it was possible to account for the observed $\Delta V^{\#}$ values on the basis of the Marcus-Hush-Stranks theoretical treatments. Application of flash-photolysis and pulse-radiolysis techniques in the study of electron-transfer reactions has been limited to specific areas of research involving the reactions of excited state species or highly reactive intermediates. In general it has been shown that electron-transfer processes in electronically excited states do exhibit characteristic pressure dependencies (for a review see ref. 1 and 6, for typical examples see ref. 37 and 38).

Flash-photolysis and pulse-radiolysis techniques have been employed very successfully in the study of long-distance electron-transfer reactions that are of biological interest (ref. 39 and 40). We have been involved in a number of studies in which the effect of pressure on intramolecular and intermolecular electron-transfer reactions of cytochrome c was investigated using the mentioned kinetic techniques (ref. 41 to 44). The intramolecular electron-transfer reactions in horse heart $(NH_3)_5Ru^{II}$-His 33 and candida krusei $(NH_3)_5Ru^{II}$-His 39 undergo significant acceleration on increasing pressure with corresponding $\Delta V^{\#}$ values of -17.7 ± 0.9 and -18.3 ± 0.7 cm^3mol^{-1}, respectively. The intermolecular process between $Ru(NH_3)_6^{2+}$ and hh cyt c exhibits a similar pressure

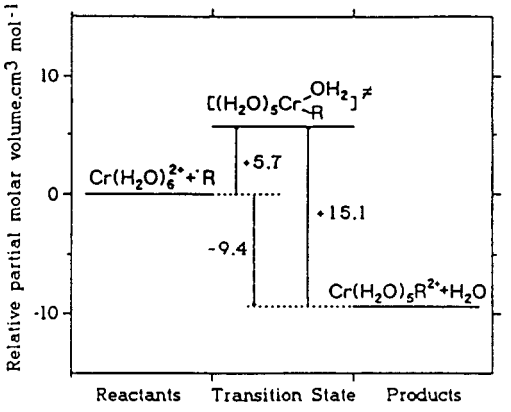


Figure 3. Volume profile for the reaction

$Cr(H_2O)_6^{2+} + \cdot C(CH_3)_2OH \rightarrow Cr(H_2O)_5C(CH_3)_2OH^{2+} + H_2O$

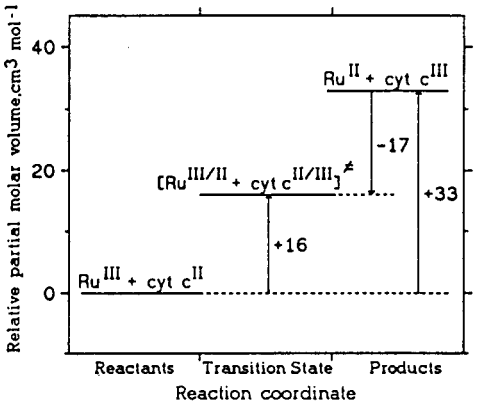


Figure 4. Volume profile for the reaction

$Ru^{III}A_5isn^{3+}$ + hh cyt $c^{II} \rightleftharpoons Ru^{II}A_5isn^{2+}$ + hh cyt c^{III}

acceleration as shown by the $\Delta V^{\#}$ data in Table 4. A qualitative interpretation of the quoted $\Delta V^{\#}$ values suggests that they mainly arise from volume changes associated with the redox behaviour of the Ru center on the surface of the protein. Intramolecular electron-transfer from cyt c to Ru(III) exhibits exactly the opposite pressure dependence than referred to above. Furthermore, our data for the intermolecular electron-transfer reaction between hh cyt c^{III} and $Ru(NH_3)_6^{2+}$ is very similar to that reported for the reaction with $Co^{II}(phen)_3^{2+}$. Again the reverse reaction exhibits the opposite trend (ref. 45). In the case of the hexacyano complexes of Fe(II/III), the observed $\Delta V^{\#}$ and $\Delta \overline{V}$ values go in the opposite direction (ref. 45) since reduction of $Fe(CN)_6^{3-}$ will be accompanied by a volume collapse and vice versa for the oxidation of $Fe(CN)_6^{4-}$. The data for the oxidation and reduction of hh cyt c by $Ru(NH_3)_5isn^{2+/3+}$ can be used to construct the overall volume profile shown in Figure 4, from which it

TABLE 4. Summary of rate and activation parameters for long distance electron-transfer reactions

Reaction [a]	k_{298}	$\Delta V^{\#}$ cm^3mol^{-1}	$\Delta \overline{V}$ cm^3mol^{-1}	Ref.
A_5Ru^{II}-hh^{III}	$39s^{-1}$	-17.7		41
A_5Ru^{II}-ck^{III}	$87s^{-1}$	-18.3		41
hh^{II}-$A_4Ru^{III}isn$	$400s^{-1}$	+4.0		44
ck^{II}-$A_4Ru^{III}isn$	$220s^{-1}$	+3.4		44
A_6Ru^{II} + hh^{III}	$6.3 \times 10^4 M^{-1}s^{-1}$	-15.6		41
hh^{II} + $A_5Ru^{III}isn$	$1.1 \times 10^5 M^{-1}s^{-1}$	+16	+33 [b], +31 [c]	42
$A_5Ru^{II}isn$ + hh^{III}	$1.5 \times 10^3 M^{-1}s^{-1}$	-17		42
hh^{II} + $Co^{III}(phen)_3^{3+}$	$1.9 \times 10^3 M^{-1}s^{-1}$	+8.5	+20	45
$Co^{II}(phen)_3^{2+}$ + hh^{III}	-	-11.5 [b]		45
hh^{II} + $Fe^{III}(CN)_6^{3-}$	$3.0 \times 10^6 M^{-1}s^{-1}$	-24 [b]	-37	45
$Fe^{II}(CN)_6^{4-}$ + hh^{III}	$1.2 \times 10^4 M^{-1}s^{-1}$	+13		45

[a] Abbreviations: A = NH_3, isn = isonicotinamide, phen = 1,10-phenanthroline

[b] Calculated from the relationship $\Delta \overline{V}$ = $\Delta V^{\#}$ (forward reaction) - $\Delta V^{\#}$ (back reaction)

[c] Measured directly from the pressure dependence of the equilibrium constant

follows that the transition state lies practically halfway between the reactant and product states on a volume basis (ref. 42). This finding is in excellent agreement with a reorganization parameter of 0.5 expected for the transition state of a highly reversible electron-transfer process. Once again the overall volume increase is quite reasonable for the reduction of Ru(III) to Ru(II) and may involve only a minor contribution from the oxidation of cytochrome c. This statement contradicts a recent report on the effect of pressure on the heterogeneous redox behavior of cytochrome c in which a volume decrease of 24 cm^3mol^{-1} was reported for the reduction of cyt c^{III} to cyt c^{II} (ref. 46).

CONCLUSIONS

The combined application of high-pressure and flash-photolysis or pulse-radiolysis techniques created the unique opportunity to look into the intimate mechanism of highly reactive intermediates and fast chemical processes. Such studies can supplement conventional kinetic measurements performed at ambient pressure, and in many cases reveal unique information about the detailed reaction mechanism. It enables us to improve our understanding of fundamental aspects of various types of chemical processes in inorganic, organometallic and bioinorganic systems. Further developments to understand fundamental processes at a molecular level, by employing higher resolution and faster spectroscopic techniques at elevated pressure, are urgently needed. Only then will a meaningful contribution to the mechanistic clarification of complex biochemical processes be possible. The application of high pressure as a kinetic parameter has been so well established by now that it has become an integral part of routine mechanistic studies.

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