

Pressure as a mechanistic indicator in substitution reactions of metal complexes

Rudi van Eldik

Institute for Inorganic Chemistry, University of Witten/Herdecke,
Stockumer Straße 10, 5810 Witten, FRG

Abstract

Substitution reactions of transition metal complexes are of fundamental importance to the understanding of many chemical and biological processes since they usually occur at the crucial point where the metal center exhibits its catalytic activity. The ability of metal complexes to bind additional ligands or to exchange their ligands according to well defined routes has stimulated many systematic studies of the mechanisms of such processes. In the past, such studies usually involved the application of conventional kinetic techniques which included systematic measurements of the concentration, ionic strength, solvent, pH and temperature dependence of such processes. Over the past decade, instrumentation has been developed that now enable kineticists to study the pressure dependence of such processes by adding an additional physical parameter to the kinetic variables. As will be shown in this contribution, ligand substitution reactions exhibit very characteristic pressure dependences such that pressure has become a reliable mechanistic indicator for such processes.

GENERAL REMARKS

Many chemical reactions that occur in solution exhibit characteristic pressure dependences. This has been well documented for reactions of transition metal complexes, usually involving ligand exchange and substitution processes.¹⁻³ In principle, it is found that reactions that involve bond formation processes are accelerated by pressure, whereas those that involve bond breakage are decelerated by pressure. The quantitative description of such pressure dependences is done in terms of the volume of activation, ΔV^\ddagger , as given in eq. (1). This quantity represents the change in partial molar volume that occurs when the reactant species move to the transition state in terms of the Eyring theory. ΔV^\ddagger will have positive or negative values

$$(\delta \ln k / \delta P)_T = -\Delta V^\ddagger / RT \quad (1)$$

depending on whether the reaction is decelerated or accelerated by increasing pressure, respectively. Such data combined with partial

molar volume measurements for reactant and product species can be employed to construct a volume profile for the reaction, i.e. to describe the chemical process in terms of volume changes along the reaction coordinate as shown in Figure 1. In general, ΔV^\ddagger may be considered as the sum of two components: an intrinsic part (ΔV_{intr}^\ddagger), which represents the change in volume due to changes in bond lengths and angles, and a solvational part (ΔV_{solv}^\ddagger), which represents the volume changes due to electrostriction and other effects acting on the surrounding solvent molecules during the activation process. It is principally the intrinsic contribution that is the mechanistic indicator in the case of substitution and related reactions. A schematic representation of these components for a typical bond formation or bond

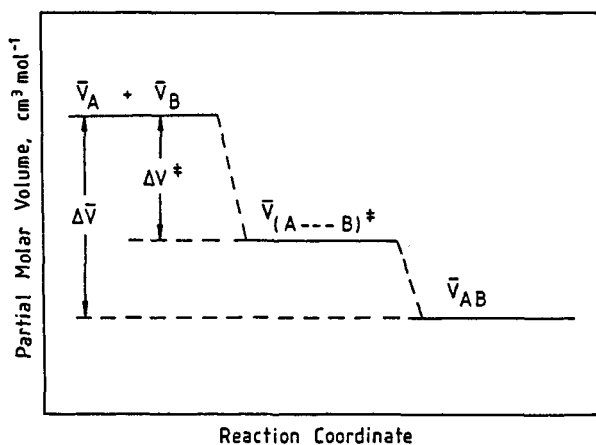


Figure 1. Volume profile for the reaction $A+B \rightleftharpoons [A---B]^\ddagger \rightarrow AB$

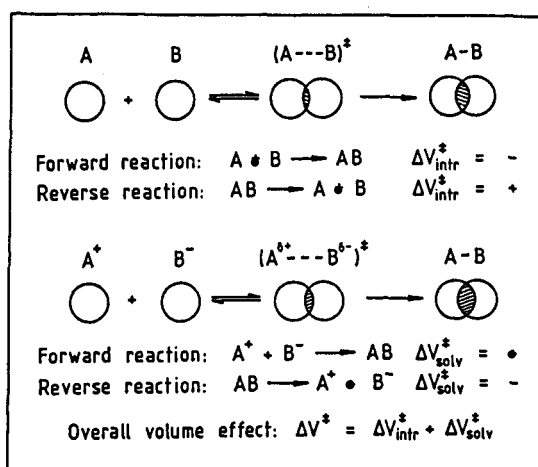


Figure 2. Schematic representation to illustrate the sign of the components of ΔV^\ddagger

cleavage process, during which partial charge neutralization or creation may occur, is given in Figure 2. The mechanistic assignment for processes in which no major solvational changes occur are, in fact, straightforward, since bond formation should result in negative ΔV_{intr}^\ddagger and bond breakage in a positive one. In reactions with large polarity changes, ΔV_{solv}^\ddagger may be larger than ΔV_{intr}^\ddagger , and it can in fact counteract and swamp the ΔV_{intr}^\ddagger term. For most of the examples discussed in this paper this is not the case, and ΔV_{exp}^\ddagger mainly represents ΔV_{intr}^\ddagger .

The pressure range adopted for such measurements goes up to 200 to 300 MPa (i.e. 2 to 3 kbar). The rapid increase in activity in this area of research is partly due to the successful development of instrumentation that enables us to perform the kinetic measurements at elevated pressures on a milli- (stopped-flow), micro- (T-jump and NMR), nano- and picosecond (pulsed laser flash photolysis) time-scale.⁴ These techniques have been applied to numerous substitution reactions of metal complexes, of which typical examples will be treated in more detail.

Most substitution reactions of metal complexes are still discussed in terms of the Langford and Gray classification.⁵ For a general ligand substitution reaction outlined in Figure 3, there are three simple pathways: (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, and in which either bond breakage (I_d) or bond formation (I_a) is the more important process. Such bond formation/bond breakage processes should be characterized by characteristic volume changes in terms of the general principles outlined above.

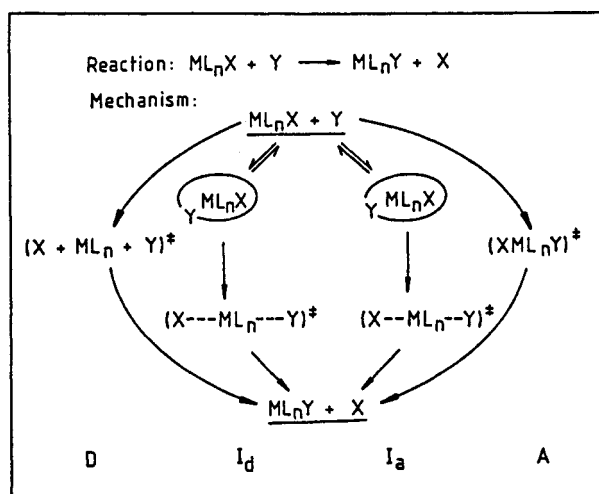


Figure 3. Schematic representation of the possible ligand substitution mechanisms

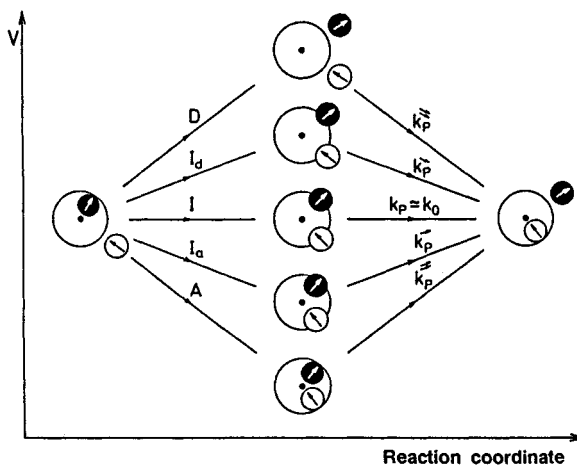


Figure 4. Schematic volume profiles for solvent exchange mechanisms⁷

SOLVENT-EXCHANGE REACTIONS

Many solvent-exchange reactions on metal complexes have been studied in recent years using high-pressure, high-resolution NMR techniques.^{6,7} For these reactions no major change in electrostriction is given by the intrinsic contribution. The volume changes associated with the various possible substitution mechanisms are schematically presented in Figure 4. A continuous spectrum of transition state configurations can be envisaged, ranging from very compact with a large negative ΔV^\ddagger value to very expanded with a large positive ΔV^\ddagger value. Typical results for solvent exchange on high spin first row divalent transition metal ions (Table I) indicate a definite trend across the series. The ΔV^\ddagger data indicate that the mechanism 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. The small positive ΔV^\ddagger found for DMF exchange on Mn^{2+} indicates that steric hindrance on the hexasolvates prevents the associative substitution mode even for the largest metal center in this

Table I. Volumes of activation ($\text{cm}^3 \text{mol}^{-1}$) for solvent S exchange on MSe^{2+} of the first row transition metal series by NMR⁷

| M^{2+} | V | Mn | Fe | Co | Ni | Cu |
|----------------------------|------------|------------------|------------------|------------------|------------------|--------------------|
| r_1 / pm | 79 | 83 | 78 | 74 | 69 | (73) ^a |
| | t_{2g}^3 | $t_{2g}^3 e_g^2$ | $t_{2g}^4 e_g^2$ | $t_{2g}^5 e_g^2$ | $t_{2g}^6 e_g^2$ | $(t_{2g}^6 e_g^3)$ |
| 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 | |
| DMF | | +2.4 | +8.5 | +9.2 | +9.1 | |
| NH_3 ^b | | | | | +5.9 | |

^a Effective ionic radius.^b In 15 M aqueous NH_3 .Table II. Rate constants and activation parameters for water exchange on some hexaqua and monohydroxypentaaqua metal ions⁷

| M^{3+} | k^{298} s^{-1} | k_{OH}/k | ΔH^\ddagger kJ mol^{-1} | ΔS^\ddagger $\text{J K}^{-1} \text{mol}^{-1}$ | ΔV^\ddagger $\text{cm}^3 \text{mol}^{-1}$ | pK _a | Mech. |
|-----------------------------|------------------------------|-------------------|---|--|--|-----------------|----------------|
| Ga^{3+} | 4.0×10^2 | 275 | 67.1 | +30.1 | +5.0 | 3.9 | I _d |
| $\text{Ga}(\text{OH})^{2+}$ | 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 |
| $\text{Fe}(\text{OH})^{2+}$ | 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 |
| $\text{Cr}(\text{OH})^{2+}$ | 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 |
| $\text{Ru}(\text{OH})^{2+}$ | 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 |
| $\text{Rh}(\text{OH})^{2+}$ | 4.2×10^{-5} | | 103.0 | - | +1.3 | | I |

bulky solvent. Such data can also distinguish between the solvent exchange mechanism for $\text{M}(\text{H}_2\text{O})_6^{3+}$ and its conjugate base $\text{M}(\text{H}_2\text{O})_5\text{OH}^{2+}$ as indicated in Table II. The higher reactivity of the hydroxo complexes is accompanied by a more dissociative character (more positive ΔV^\ddagger), i.e. a trans-labilization effect of the hydroxy ligand.

LIGAND SUBSTITUTION REACTIONS

Many substitution reactions are non-symmetrical, i.e. the reactant and product species are different, and the overall reaction volume is usually not zero. However, mechanistic similarities are expected to occur for ligand substitution as compared to solvent-exchange reactions. A summary of the data available for complex formation reactions of divalent first-row transition metal elements (Table III), clearly

Table III. ΔV^\ddagger for the interchange of neutral and uninegative ligands on M^{2+} ions in water⁶

| Ligand ^a | V ²⁺ | Mn ²⁺ | Fe ²⁺ | Co ²⁺ | Ni ²⁺ | Cu ²⁺ | Zn ²⁺ |
|---------------------|-----------------|------------------|------------------|------------------|------------------|------------------|------------------|
| H ₂ O | -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.

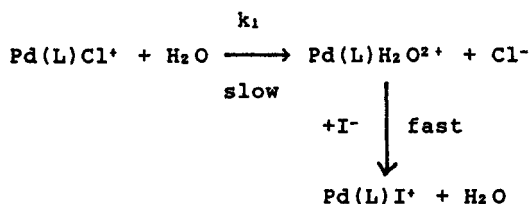
demonstrates the same trend as for the water-exchange reactions, i.e. a gradual mechanistic changeover from I_a to I_d along the series. Another exciting example involves the aquation reactions of pentaammine complexes of Co(III) and Cr(III) involving a series of neutral leaving groups.⁸ The reported ΔV^\ddagger data are in excellent agreement with the water-exchange data and support the operation of an I_a mechanism in the case of the Cr(III) complexes compared to an I_d mechanism in the case of the Co(III) complexes.

The so far discussed solvent-exchange and ligand substitution reactions were all characterized by relatively small ΔV^\ddagger values in line with the concept of an interchange mechanism. We will now consider some examples to demonstrate the magnitude of ΔV^\ddagger for limiting D and A mechanisms. Aquation reactions of pentacyanoiron(II/III) complexes exhibit ΔV^\ddagger values ranging from +16 to +27 cm³ mol⁻¹, which support a D mechanism.⁹⁻¹¹ At the other end of the scale, ΔV^\ddagger values between -14 and -17 cm³ mol⁻¹ were reported for ligand substitution on Rh^I(Cp)(CO)₂ which is generally accepted to proceed according to an associative ring-slippage mechanism.¹² Thus the limiting ligand substitution mechanisms are characterized by ΔV^\ddagger values of a significantly larger absolute magnitude than the interchange processes. Having developed a feeling for the meaning of ΔV^\ddagger in terms of well-understood ligand substitution processes, it is now possible to consider a couple of examples in which such data has assisted the elucidation of the intimate mechanism.

For ligand exchange and substitution reactions of square planar d⁸ metal complexes it is generally assumed that substitution follows an A mechanism.¹³ A fundamental question that has often been raised in the

literature concerns the possibility to force such reactions to proceed via a dissociative mechanism by increasing the steric hindrance on the non-exchanging ligands. The data in Table IV nicely demonstrate that the introduction of steric hindrance on the dien ligand decreases the aquation rate constant by up to six orders of magnitude, but does not affect the nature of the substitution mechanism as evidenced by the significantly negative ΔS^\ddagger and ΔV^\ddagger values throughout the series of complexes. A similar result was obtained for water-exchange on complexes of the type $\text{Pd}(\text{R}_5\text{dien})\text{H}_2\text{O}^{2+}$.⁷ From these results it can be concluded that steric hindrance alone cannot cause a changeover in mechanism for ligand substitution reactions of square planar complexes. Recent reports¹⁴ have, however, indicated that a changeover in mechanism can be achieved via electronic effects, for instance trans-labilization of the Pt-C bond can induce a dissociative ligand exchange process.¹⁵

Table IV. Kinetic parameters for the reaction ¹³



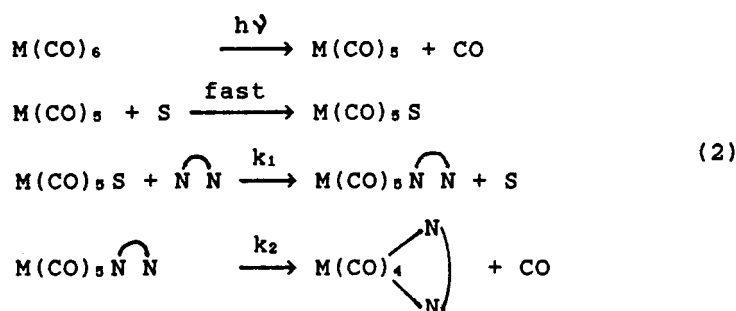
| L | k_1 at 25 °C s ⁻¹ | ΔH^\ddagger kJ mol ⁻¹ | ΔS^\ddagger J K ⁻¹ mol ⁻¹ | ΔV^\ddagger at 25 °C cm ³ mol ⁻¹ |
|------------------------------------|-----------------------------------|---|--|---|
| dien * | 43.8 ± 0.5 | 43±3 | -69±12 | -10.0±0.6 |
| 1,4,7-Me ₃ dien | 25.0 ± 4.2 | 38±4 | -87±15 | -9.2±0.6 |
| 1,4,7-Et ₃ dien | 10.0 ± 0.1 | 41±5 | -86±18 | -10.8±1.0 |
| 1,1,7,7-Me ₄ dien | 0.99±0.02 | 49±1 | -79± 3 | -13.4±1.9 |
| 1,1,4-Et ₃ dien | 0.77±0.01 | 51±1 | -76± 3 | -14.5±1.2 |
| 1,1,4,7,7-Me ₅ dien | (2.76±0.04)×10 ⁻¹ | 50±1 | -88± 3 | -10.9±0.3 |
| 1,1,7,7,-Et ₄ dien | (2.1 ± 0.4)×10 ⁻³ | 69±2 | -67± 8 | -14.9±0.2 |
| 4-Me-1,1,7,7,-Et ₄ dien | (6.8 ± 0.1)×10 ⁻⁴ | 66±7 | -84±25 | -14.3±0.6 |
| 1,1,4,7,7-Et ₅ dien | (6.7 ± 0.1)×10 ⁻⁴ | 59±3 | -106± 9 | -12.8±0.8 |

* diethylenetriamine

PHOTO-INDUCED SUBSTITUTION REACTIONS

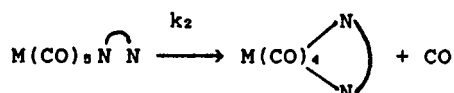
It was demonstrated above that thermal ligand exchange and substitution reactions exhibit characteristic pressure dependencies. Flash photolysis techniques have in general been adopted with great success to study the substitution behaviour of reactive intermediates in organometallic chemistry. Irradiation of $\text{M}(\text{CO})_6$ (M = Cr, Mo, W) in a coordinating solvent S produces intermediates of the type $\text{M}(\text{CO})_5\text{S}$, which can undergo

rapid subsequent ligand substitution with a nucleophile L to produce $M(CO)_5L$. The pressure dependence of such substitution reactions has been studied for a series of M, S and L, and the results once again demonstrate the crucial role played by the size of the metal center and the bulkiness of the ligand.^{16,17} When the attacking nucleophile is a bidentate ligand, flash photolysis results in the reaction sequence outlined in (2).



Kinetic data for a series of ring-closure reactions (k_2) are summarized in Table V, from which it follows that k_2 can vary by nine orders of magnitude depending on the nature of NN. The highly structured ligand 1,10-phenanthroline undergoes rapid ring-closure for which k_2 exhibits different pressure dependences depending on M (see Figure 5). In contrast, ethylenediamine is free to move and ring-closes very slowly in an associative way according to the ΔV^\ddagger data in Table V. It follows that the larger metal centers Mo and W can undergo associative ring-closure, whereas the smaller metal center Cr undergoes dissociative

Table V. Summary of available data for ring-closure reactions^{18,19}



| M | Solvent | $\overset{\curvearrowright}{N-N}$ | k_2 at 25 °C s ⁻¹ | ΔH^\ddagger kJ mol ⁻¹ | ΔS^\ddagger J K ⁻¹ mol ⁻¹ | ΔV^\ddagger cm ³ mol ⁻¹ |
|----|---------|-----------------------------------|-----------------------------------|---|--|--|
| Cr | Tol | en | 1.6×10^{-5} | 57 ± 5 | -145 ± 17 | -11.9 ± 1.5 |
| | Tol | dabR ₂ * | 1.5×10^{-4} | 81 ± 2 | -47 ± 7 | $+17.2 \pm 1.0$ |
| | FB | phen | 26 | 52 ± 2 | -42 ± 6 | $+6.2 \pm 0.5$ |
| Mo | Tol | en | 3.0×10^{-5} | 72 ± 7 | -92 ± 22 | -5.4 ± 0.8 |
| | Tol | dabR ₂ * | 1.1×10^{-3} | 78 ± 5 | -40 ± 17 | -9.5 ± 0.4 |
| | FB | phen | 1.1×10^4 | 47 ± 2 | -9 ± 7 | -2.9 ± 0.2 |
| W | Tol | en | 3.0×10^{-6} | 54 ± 5 | -172 ± 16 | -12.3 ± 1.4 |
| | Tol | dabR ₂ * | 2.9×10^{-5} | 83 ± 8 | -53 ± 26 | -13.7 ± 1.3 |
| | Tol | bpy | 8.0×10^{-2} | 58 ± 2 | -74 ± 7 | -10.9 ± 1.1 |
| | FB | phen | 432 | 51 ± 2 | -23 ± 5 | -8.2 ± 0.2 |

* R = i-Pr

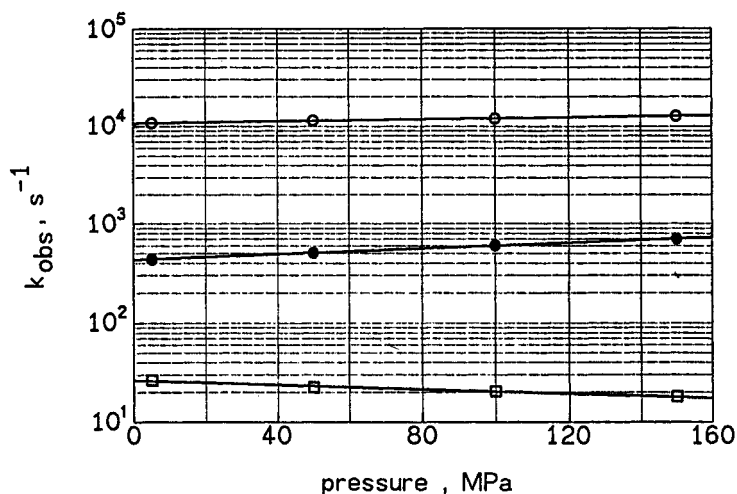


Figure 5. Plot of $\log k_{obs}$ vs pressure for ring-closure of $M(CO)_5phen$. Top to bottom: $M = Mo, W, Cr$

ring-closure for the bulkier chelating ligands. Only in the case of ethylenediamine is the Cr center capable to ring-close in an associative way. It follows that there is a fine tuning effect between the size of the central metal atom and the bulkiness of the entering ligand in determining the nature of the substitution mechanism in such systems.

PHOTOCHEMICAL SUBSTITUTION REACTIONS

Earlier work has shown that chemical and physical processes that occur in the electronic excited state of inorganic and organometallic complexes exhibit characteristic pressure dependences.^{1,2} Is it possible to use this information to elucidate the nature of a ligand substitution process in the excited state of a molecule? To demonstrate this, the CO photosubstitution in $M(CO)_4phen$ ($M = Cr, Mo, W$) was selected.^{20,21} 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. On the other hand it was argued that the MLCT states themselves are photoactive and could undergo photosubstitution. The pressure dependence of the quantum yield for the photosubstitution was measured as a function of irradiation wavelength, and some typical results are reported in Figure 6. The corresponding volumes of activation are summarized in Table VI, from which it follows that in the Mo and W complexes MLCT and LF photosubstitution occur according to associative and dissociative mechanisms, respectively. For the smaller Cr complex the associative MLCT path does not seem to be possible and even this reaction has to follow a dissociatively activated process, presumably of the interchange type

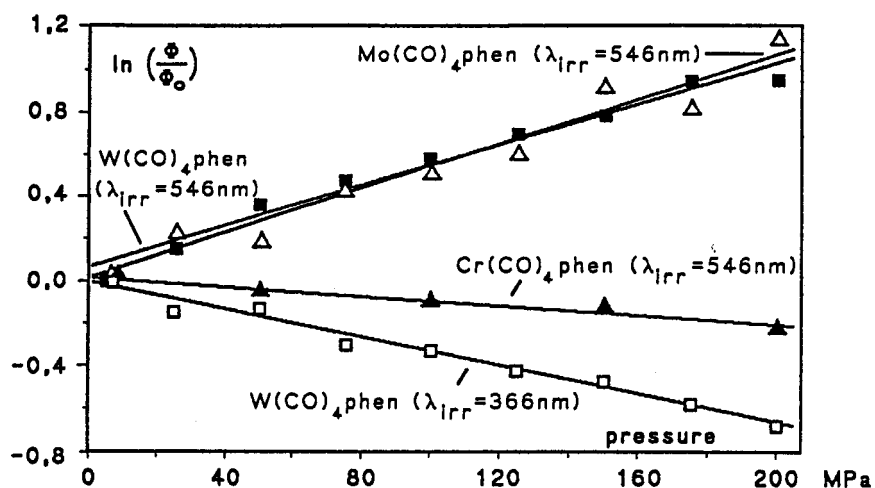


Figure 6. Pressure dependence of the quantum yield of the reaction $M(\text{CO})_4\text{phen} + \text{PET}_3 \xrightarrow{h\nu} M(\text{CO})_3(\text{PET}_3)\text{phen} + \text{CO}$ in toluene²⁰

Table VI. Quantum yields and volumes of activation for the reaction²¹

$$M(\text{CO})_4\text{phen} + \text{PET}_3 \xrightarrow{h\nu} M(\text{CO})_3(\text{PET}_3)\text{phen} + \text{CO}$$

Toluene

| M | [PET ₃] M | λ_{irr} nm | ϕ_0 | ΔV^\ddagger (MLCT) | $\Delta V^\ddagger_{\text{e}}/(1-\phi)$ (LF) |
|----|--------------------------|------------------------------|--------------------|-------------------------------|---|
| Cr | 0.0128 | 366 | 0.55 | | +9.6 ± 1.6 |
| | 0.0135 | 546 | 0.11 ^a | +2.7 ± 0.3 | |
| Mo | 0.0128 | 366 | 0.056 | | +6.0 ± 0.2 |
| | 0.135 | 546 | 0.010 ^b | -13.3 ± 1.2 | |
| W | 0.0135 | 366 | 0.018 | | +8.2 ± 0.5 |
| | 0.135 | 546 | 0.006 ^b | -12.0 ± 0.7 | |

^a ϕ independent of [PET₃]

^b ϕ depends on [PET₃]

(Id). These results nicely underline the value of pressure as a key parameter to distinguish between associative and dissociative photo-substitution mechanisms.

CONCLUDING REMARKS

It was the intention of this contribution to demonstrate that pressure can be a useful physical parameter in mechanistic studies of ligand substitution reactions of metal complexes. It can complete the comprehension of chemical kinetics by supplying additional and/or rather unique information that assists the assignment of the intimate mechanism and so contributes toward a better understanding of the chemical process. Although this contribution solely focussed on thermal and

photochemical substitution reactions, similar data are presently available for almost any kind of chemical process in inorganic, organometallic and bioinorganic systems.^{2,3}

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