

107. High-Pressure, High-Resolution Nuclear Magnetic Resonance (HPHR-NMR.): A Tool in Chemical Kinetics¹⁾

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Summary

In recent years the volume of activation ΔV^* has become a powerful tool in chemical kinetics. High resolution NMR. spectroscopy is now one of the most common techniques used in the study of the kinetics of labile chemical systems. In order to measure ΔV^* by this technique, we have built a ¹H-probe-head, for a *Fourier* transform spectrometer, working up to 4 kbar and with a resolution of 0.6 Hz. The temperature is regulated and measured with an accuracy better than 0.2°. The high pressure probe-head has been tested on a chemical system showing a dissociative-associative crossover for the ligand substitution mechanism. It had been shown previously that the ligand exchange $\text{TaBr}_5 \cdot \text{L} + * \text{L} \rightleftharpoons \text{TaBr}_5 \cdot * \text{L} + \text{L}$ proceeds *via* a *D* mechanism when $\text{L} = \text{Me}_2\text{O}$, and *via* an *I_a* mechanism when $\text{L} = \text{Me}_2\text{S}$. As expected, ΔV_0^* is positive ($+30.5 \pm 2.0 \text{ cm}^3 \text{ mol}^{-1}$) for the dissociative process and negative ($-12.6 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$) for the associative one.

Kinetic measurements at various pressures led in transition state theory to the volume of activation ΔV^* . In recent years this activation parameter has become a powerful tool in chemical kinetics, because the interpretation of a volume change is usually simple to handle and to associate with a reaction mechanism. It is currently used to diagnose dissociative and associative substitution processes [1] [2]. High resolution NMR. spectroscopy is one of the most common techniques used in the study of the kinetics of labile chemical systems [3]. The phenomena currently studied involve for example: intermolecular exchange processes, polytopal rearrangements, fast conformational flips, etc. Few HPHR-NMR. systems have been described. They have been used [4] mainly to study molecular dynamics and structures by means of chemical shifts or T_1 measurements. In order to apply HPHR-NMR. to the field of chemical kinetics we have built an NMR. probe-head working at elevated pressures, with the

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high spectral resolution and good temperature stability and accuracy required for such applications. To our knowledge, we report the first NMR. measurements of volumes of activation, ΔV_0^* .

Our probe-head works up to pressures of 4 kbar and with a resolution of 0.6 Hz for 1 scan, and 1 Hz with accumulation. It is built for a *Bruker* WP-60 spectrometer and has the same dimensions as the commercial one sold for work at atmospheric pressure. The sample is contained in a non-spinning glass capillary tube of 1.2 mm i. d. The temperature is regulated and measured with an accuracy of $\pm 0.2^\circ$.

To test our high pressure probe-head we have chosen a chemical system showing a dissociative-associative crossover for the ligand substitution mechanism. It has been shown previously [5] that the ligand exchange reaction $\text{MX}_5 \cdot \text{L} + \text{*L} \rightleftharpoons \text{MX}_5 \cdot \text{*L} + \text{L}$ for the octahedral adducts $\text{MX}_5 \cdot \text{L}$ ($\text{M} = \text{Nb}, \text{Ta}$; $\text{X} = \text{Cl}, \text{Br}$) proceeds *via* a dissociative *D* mechanism when $\text{L} = \text{Me}_2\text{O}$, and *via* an interchange associative *I_a*

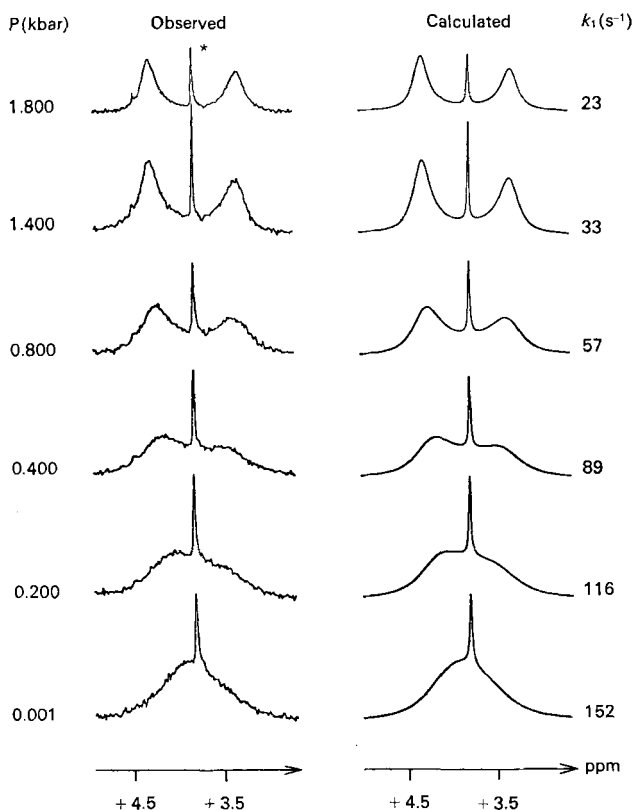


Fig. 1. Observed and calculated $^1\text{H-NMR}$. spectra for the *D* ligand exchange $\text{TaBr}_5 \cdot \text{Me}_2\text{O} + \text{*Me}_2\text{O} \rightleftharpoons \text{TaBr}_5 \cdot \text{*Me}_2\text{O} + \text{Me}_2\text{O}$ as a function of pressure, in CH_2Cl_2 at 286.1 K. (*) = signal of the ^{13}C satellite of the solvent. ($[\text{TaBr}_5 \cdot \text{Me}_2\text{O}] = 0.130 \text{ m}$, $[\text{Me}_2\text{O}] = 0.114 \text{ m}$; $\delta(\text{TaBr}_5 \cdot \text{Me}_2\text{O}) = 4.36 \text{ ppm}$, $\delta(\text{Me}_2\text{O}) = 3.33 \text{ ppm}$).

mechanism when $L = \text{Me}_2\text{S}$, Me_2Se , Me_2Te . In this preliminary communication we present one example of each of these two types of substitution.

In the adduct of tantalum bromide with dimethyloxide, which reacts *via* a D mechanism (1st order rate law, $\Delta H^* = 17.8 \pm 0.8 \text{ kcal mol}^{-1}$, $\Delta S^* = +15.3 \pm 3 \text{ cal K}^{-1} \text{ mol}^{-1}$), the ligand exchange rate should be slowed down with increasing pressure because the bond breaking process involves an increase in volume at the transition state. At low pressure the exchange is fast and it slows down with increasing pressure (Fig. 1). At high pressure one can see the two resonances of free and coordinated dimethyloxide. The good resolution and signal to noise ratio can be seen from the signal of the ^{13}C satellite of the dichloromethane solvent. The rate constants, k , were obtained by line-shape analysis and $\ln k$ was fitted *vs.* pressure to a quadratic equation. The volume of activation at zero pressure $\Delta V_0^* = +30.5 \pm 2.0 \text{ cm}^3 \text{ mol}^{-1}$ has been obtained with excellent accuracy.

In the adduct of tantalum bromide with dimethylsulfide, which reacts *via* an I_a mechanism (2nd order rate law, $\Delta H^* = 6.9 \pm 0.4 \text{ kcal mol}^{-1}$, $\Delta S^* = -24 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$) we have the inverse situation involving the formation of a new bond, with contraction as the reacting molecules approach each other in the transition state. As expected, the change in the spectra (Fig. 2) is just the reverse of the change observed

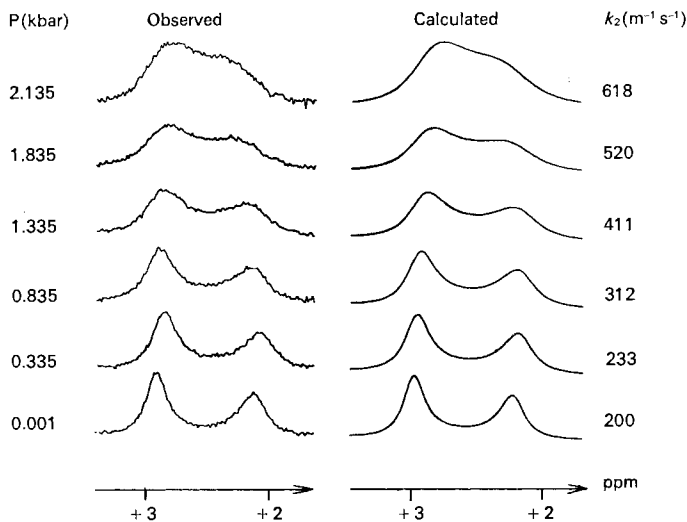


Fig. 2. Observed and calculated $^1\text{H-NMR}$ spectra for the I_a ligand exchange $\text{TaBr}_5 \cdot \text{Me}_2\text{S} + * \text{Me}_2\text{S} \rightleftharpoons \text{TaBr}_5 \cdot * \text{Me}_2\text{S} + \text{Me}_2\text{S}$ as a function of pressure, in CH_2Cl_2 at 285.6 K. ($[\text{TaBr}_5 \cdot \text{Me}_2\text{S}] = 0.160 \text{ m}$, $[\text{Me}_2\text{S}] = 0.131 \text{ m}$; $\delta(\text{TaBr}_5 \cdot \text{Me}_2\text{S}) = +2.94 \text{ ppm}$, $\delta(\text{Me}_2\text{S}) = +2.13 \text{ ppm}$).

for the D reaction of dimethyloxide. At normal pressure, the resonances of the free and coordinated ligand are observed. With increasing pressure, the rate for the I_a exchange process increases and one observes a coalescence with a broad signal at 2.135 kbar. ΔV_0^* is therefore negative with a value of $-12.6 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$. It is instructive to compare the accuracy given for ΔS^* and ΔV_0^* . As already claimed by

other investigators [1], it is clear that volumes of activation can be measured more accurately than entropies of activation.

For neutral intermolecular ligand exchange reactions there is no important development of charge on going to the transition state. Therefore, the electrostrictive contribution to ΔV_0^* will be small and can be neglected with respect to the structural contribution. This situation will usually be met in systems studied by NMR., giving a straightforward interpretation.

The strongly positive ΔV_0^* value for the dimethyloxy exchange reaction on the tantalum pentabromide adduct, and the negative value for the dimethylsulfide exchange reaction confirm the *D* and *I_a* mechanism proposed earlier. The quantitative interpretation of these first ΔV_0^* values obtained by HPHR-NMR. must await further results for other similar systems.

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