

# Variable-pressure $^1\text{H}$ NMR studies of hexamethylphosphoramide and trimethyl phosphate exchange on dioxouranium(VI)

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## Abstract

By extending the variable pressure  $^1\text{H}$  NMR studies to the actinides, volumes of activation and new variable-temperature activation parameters are obtained for solvent exchange in  $\text{CD}_2\text{Cl}_2$  diluent for  $[\text{UO}_2(\text{HMPA})_4]^{2+}$ :  $k_2$  (273 K) =  $40.4 \pm 3 \text{ kg mol}^{-1} \text{ s}^{-1}$ ,  $\Delta H_2^\ddagger = 47.1 \pm 3 \text{ kJ mol}^{-1}$ ,  $\Delta S_2^\ddagger = -41.0 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta V_2^\ddagger = -11.3 \pm 1.4 \text{ cm}^3 \text{ mol}^{-1}$ , and for  $[\text{UO}_2(\text{TMPA})_5]^{2+}$ :  $k_1$  (260 K) =  $55.7 \pm 3 \text{ s}^{-1}$ ,  $\Delta H_1^\ddagger = 44.1 \pm 2 \text{ kJ mol}^{-1}$ ,  $\Delta S_1^\ddagger = -40.7 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta V_1^\ddagger = +2.1 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$ . These new rate parameters which complete our earlier studies, indicate the operation of A and D mechanisms for exchange of HMPA and TMPA, respectively, on the dioxouranium(VI) ion.

## Introduction

The activation volume,  $\Delta V^\ddagger$ , has been shown to be a powerful parameter in mechanistic assignment for solvent exchange and ligand substitution processes on a large range of metal centres [1–7]. In cases where it is possible to vary the concentrations of coordinating solvent through the addition of an inert diluent, the mechanistic deductions arising from the solvent exchange rate laws and activation volumes have been in excellent agreement as exemplified by the exchange of dimethyl sulfoxide and tetramethylurea on beryllium(II) [8] and dimethylformamide on the eight-coordinate trivalent lanthanides [9].

The aim of this work is to extend our variable-pressure studies to the actinides through a study of solvent exchange on dioxouranium(VI). In the solid state, this species is characterized by two oxo ligands bound in axial sites with averaged axial U–O distances in the range 1.71–1.75 Å, and four or five oxygen donor solvent molecules occupying the equatorial plane characterized by averaged equatorial distances of 2.27 Å in  $[\text{UO}_2(\text{HMPA})_4]^{2+}$  (HMPA = hexamethylphosphoramide) [10], and by averaged equatorial distances [11, 12] of 2.38 and 2.45 Å in  $[\text{UO}_2(\text{DMSO})_5]^{2+}$  (DMSO = dimethyl sulphoxide) and  $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ . In solution the two oxo atoms undergo exchange very slowly, while the equatorial solvent molecules undergo exchange

within the NMR timescale and thus the  $[\text{UO}_2(\text{solvent})_n]^{2+}$  systems offer the unusual opportunity to study solvent exchange in a single plane of a solvated metal ion.

The two systems  $[\text{UO}_2(\text{HMPA})_4]^{2+}$  and  $[\text{UO}_2(\text{TMPA})_5]^{2+}$  (TMPA = trimethyl phosphate) have been selected for study as they are characterized by different coordination numbers and different solvent exchange rate laws in  $\text{CD}_2\text{Cl}_2$  diluent [13, 14] as shown in eqns. (1) and (2)

$$\begin{aligned} \text{exchange rate} &= k_{\text{ex}} \times 4[\text{UO}_2(\text{HMPA})_4]^{2+} \\ &= (k_1 + k_2[\text{HMPA}]) \times 4[\text{UO}_2(\text{HMPA})_4]^{2+} \end{aligned} \quad (1)$$

$$\begin{aligned} \text{exchange rate} &= k_{\text{ex}} \times 5[\text{UO}_2(\text{TMPA})_5]^{2+} \\ &= k_1 \times 5[\text{UO}_2(\text{TMPA})_5]^{2+} \end{aligned} \quad (2)$$

In these equations  $k_{\text{ex}}$ ,  $k_1$  and  $k_2$  characterize a single coordinated solvent molecule and  $k_{\text{ex}}$  is the rate constant determined at a given concentration, and  $k_1$  and  $k_2$  characterize first and second order exchange terms which have been assigned to D and A mechanisms.

## Experimental

### Materials and preparation of solutions

$[\text{UO}_2(\text{HMPA})_4](\text{ClO}_4)_2$  and  $[\text{UO}_2(\text{TMPA})_5](\text{ClO}_4)_2$  were prepared according to the methods described in the literature [13, 14]. The purity of the complexes was

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TABLE 1. Kinetic parameters for ligand exchange on  $\text{UO}_2(\text{solvent})_n^{2+}$  in  $\text{CD}_2\text{Cl}_2$  diluent

	$\text{UO}_2(\text{HMPA})_4^{2+ \text{ a}}$		$\text{UO}_2(\text{TMPA})_5^{2+ \text{ c}}$
$k_2^{298}$ ( $\text{kg mol}^{-1} \text{ s}^{-1}$ )	$251 \pm 22$ (431) <sup>b</sup>	$k_1^{298}$ ( $\text{s}^{-1}$ )	$873 \pm 48$ (492) <sup>d</sup>
$\Delta H_2^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$47.1 \pm 3$ (22) <sup>b</sup>	$\Delta H_1^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$44.1 \pm 2$ (25) <sup>d</sup>
$\Delta S_2^\ddagger$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$-41.0 \pm 9$ ( $-120$ ) <sup>b</sup>	$\Delta S_1^\ddagger$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$-40.7 \pm 6$ ( $-109$ ) <sup>d</sup>
$\Delta V_2^\ddagger$ (304 K) ( $\text{cm}^3 \text{ mol}^{-1}$ )	$-11.3 \pm 1.4^e$	$\Delta V_1^\ddagger$ (280 K) ( $\text{cm}^3 \text{ mol}^{-1}$ )	$+2.1 \pm 1.5^e$

<sup>a</sup> $[\text{UO}_2(\text{HMPA})_4^{2+}] = 0.092 \text{ m}$ ,  $[\text{HMPA}] = 0.386 \text{ m}$ , for variable-temperature (245–313 K) and variable-pressure studies. The density of the  $\text{CD}_2\text{Cl}_2$  diluent is  $1.372 \text{ g cm}^{-3}$ . The contribution of second order term ( $k_2[\text{HMPA}]/\text{s}^{-1}$ ) is of 93.3% of the rate constant  $k_{\text{ex}}$  at the highest temperature of this study. <sup>b</sup>Ref. 13. <sup>c</sup> $[\text{UO}_2(\text{TMPA})_5^{2+}] = 0.0370$  and  $0.0311 \text{ m}$ ,  $[\text{TMPA}] = 0.188$  and  $0.182 \text{ m}$ , for variable-temperature (240–306 K) and variable-pressure studies, respectively. <sup>d</sup>Ref. 14. <sup>e</sup>Linear fits values are:  $-9.9 \pm 0.4$  and  $+0.6 \pm 0.3$ , and those of quadratic fits:  $-12.6 \pm 0.7$  and  $+3.5 \pm 0.5$  for HMPA and TMPA systems respectively, of  $\ln k$  vs. pressure [18].

checked by elementary analysis. In solution, the coordination numbers of the  $[\text{UO}_2(\text{HMPA})_4]^{2+}$  and  $[\text{UO}_2(\text{TMPA})_5]^{2+}$  species were obtained by integration of the free and bound  $^1\text{H}$  NMR signals of the corresponding ligands, and were found to be  $3.8 \pm 0.2$  and  $4.9 \pm 0.2$ , respectively.

The solutions of  $[\text{UO}(\text{HMPA})_4](\text{ClO}_4)_2$  and HMPA, and  $[\text{UO}_2(\text{TMPA})_5](\text{ClO}_4)_2$  and TMPA in  $\text{CD}_2\text{Cl}_2$  diluent (Armar 99.6%) (Table 1), were prepared under dry nitrogen. Each solution was transferred to a 5 mm o.d. NMR tube and was degassed on a vacuum line prior to sealing under vacuum not more than 1 h before commencement of the NMR experiment. HMPA, TMPA and  $\text{CD}_2\text{Cl}_2$  were dried and distilled under reduced vacuum prior to use [15]. All concentrations are expressed in moles per kilogram of diluent ( $m = \text{mol kg}^{-1}$ ).

#### NMR measurements

Ambient pressure  $^1\text{H}$  NMR spectra were run on a Bruker AC-200 spectrometer (cryomagnet 4.7 T) working at 200 MHz. The internal  $^1\text{H}$  NMR chemical shift reference was 5% wt./wt. TMS. The temperature was measured before and after spectral accumulation by substituting the sample with a Pt-100 resistance and was  $\pm 0.2 \text{ K}$ .

Spectra at variable pressure were run on a Bruker AM-400 spectrometer working at 400 MHz. Deuterated dichloromethane ( $\text{CD}_2\text{Cl}_2$ ) was used as an inert diluent as well as an internal lock substance. 5%  $\text{CH}_2\text{Cl}_2$  was used as an internal linewidth and a chemical shift reference. Measurements were made up to 200 MPa using a home-built high-pressure probe, which has previously been described [16]. A built-in platinum resistor allows temperature measurements with an accuracy of 1 K after all corrections, using a program derived from EXCNG [17]. By pumping thermostated synthetic oil through the bomb, the temperature was stabilized to  $\pm 0.2 \text{ K}$ .

#### Computation method

The rate constants reported were calculated from line-broadened spectra and were treated by a complete lineshape analysis based on the Kubo-Sack formalism, using modified Bloch equations [17]. The analysis of the experimental data using the required equations was done by a non-linear least-squares program fitting the desired parameter values. Reported errors are one standard deviation.

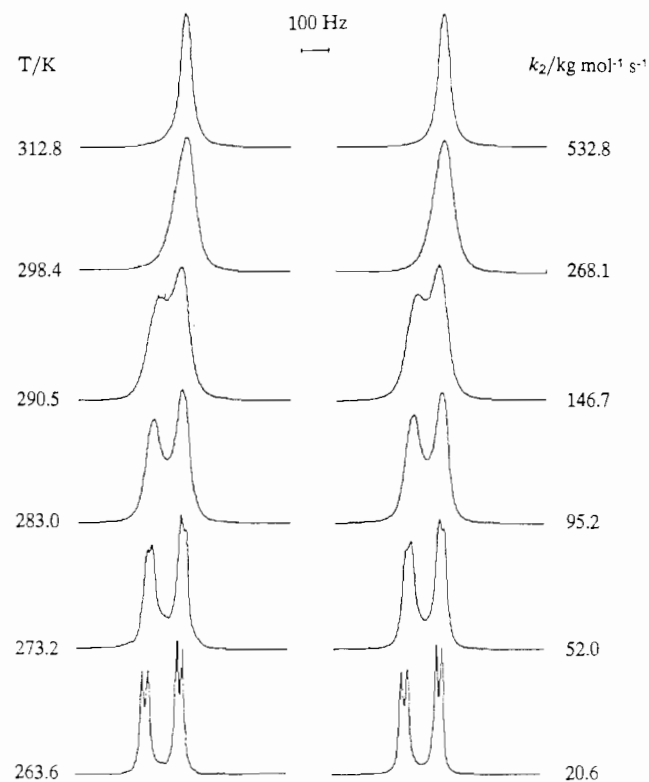


Fig. 1. Experimental (left side) and simulated 200 MHz  $^1\text{H}$  NMR line shapes of a  $\text{UO}_2(\text{HMPA})_4^{2+}$  ( $0.092 \text{ mol kg}^{-1}$ ), HMPA ( $0.386 \text{ mol kg}^{-1}$ ),  $\text{CD}_2\text{Cl}_2$  solution. Experimental temperatures (K) and best-fit  $k_2$  ( $\text{kg mol}^{-1} \text{ s}^{-1}$ ) values appear on the left and right sides of the Figure, respectively.

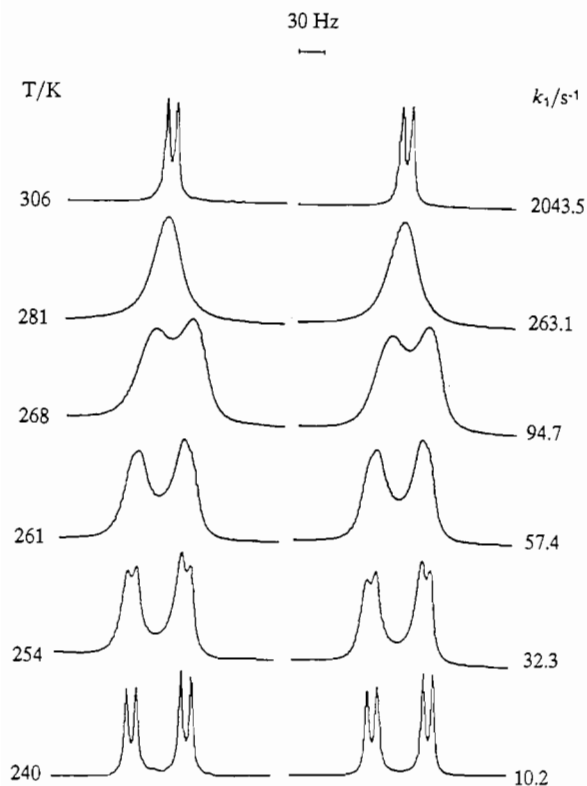


Fig. 2. Experimental (left side) and simulated 200 MHz  $^1\text{H}$  NMR line shapes of a  $\text{UO}_2(\text{TMPA})_5^{2+}$  ( $0.037 \text{ mol kg}^{-1}$ ),  $\text{TMPA}$  ( $0.188 \text{ mol kg}^{-1}$ ),  $\text{CD}_2\text{Cl}_2$  solution. Experimental temperatures (K) and best-fit  $k_1$  ( $\text{s}^{-1}$ ) values appear on the left and right sides of the Figure, respectively.

## Results and discussion

The kinetic parameters derived from our variable-temperature (Figs. 1 and 2) and variable-pressure (Figs. 3 and 4) solvent exchange studies of  $[\text{UO}_2(\text{HMPA})_4]^{2+}$  and  $[\text{UO}_2(\text{TMPA})_5]^{2+}$  appear in Table 1 together with those derived in earlier studies. Where differences appear between data sets for the same system it is anticipated that the parameters arising from the new data should be more accurate due to the larger chemical shifts between the free and bound solvent resonances obtained at 200 MHz by comparison to those obtained at 90 MHz in the earlier studies, and possibly the improved temperature calibration procedure [13, 14].

The negative  $\Delta V^\ddagger$  obtained for the  $k_2$  path for exchange on  $[\text{UO}_2(\text{HMPA})_4]^{2+}$  is consistent with the assignment of an A mechanism to this exchange process. However,  $\Delta V^\ddagger$  is only a small fraction of the partial molar volume of HMPA, calculated from the density of the pure solvent,  $V_s^\circ = 175.0 \text{ cm}^3 \text{ mol}^{-1}$ , which suggests that as the entering HMPA forms the fifth equatorial bond in the transition state, the other four bound HMPA move outwards to occupy more space so that the decrease in volume anticipated for the bonding of

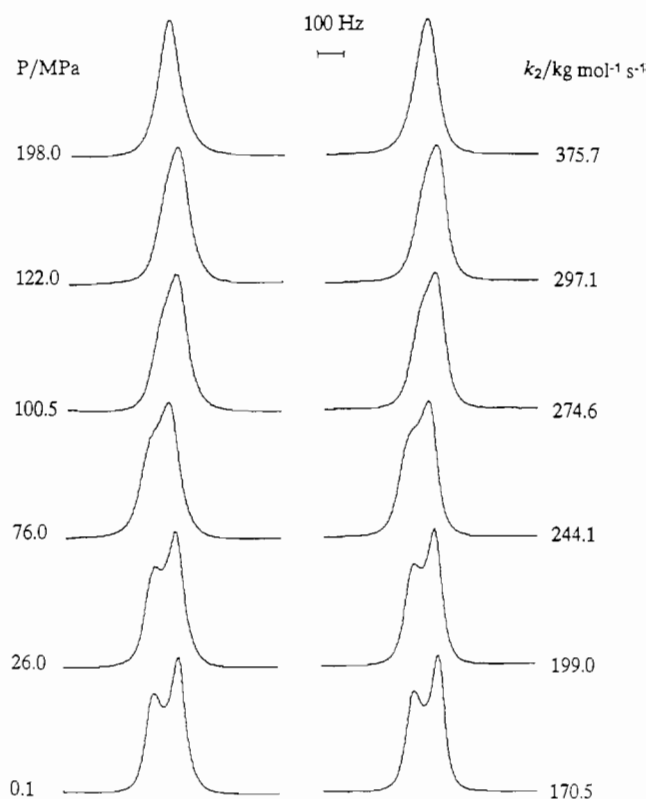


Fig. 3. Experimental (left side) and simulated 400 MHz  $^1\text{H}$  NMR line shapes of a  $\text{UO}_2(\text{HMPA})_4^{2+}$  ( $0.092 \text{ mol kg}^{-1}$ ),  $\text{HMPA}$  ( $0.386 \text{ mol kg}^{-1}$ ),  $\text{CD}_2\text{Cl}_2$  solution at 304 K. Experimental pressures (MPa) and best-fit  $k_2$  ( $\text{kg mol}^{-1} \text{ s}^{-1}$ ) values appear on the left and right sides of the Figure, respectively.

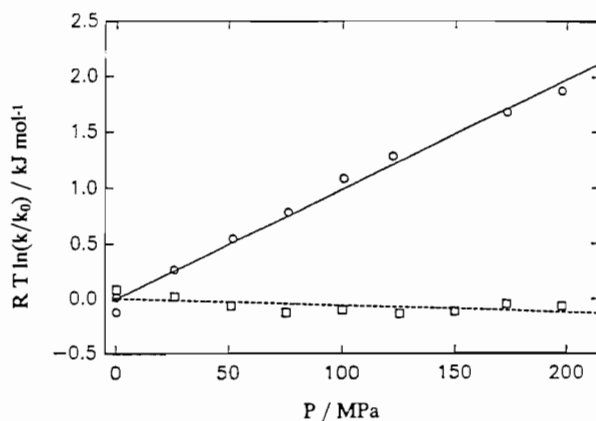


Fig. 4. Influence of pressure on the solvent exchange rate of  $\text{UO}_2(\text{solvent})_n^{2+}$ . The data for HMPA and TMPA appear as  $\circ$  and  $\square$ , respectively (linear fits of the data).

the entering ligand is substantially counterbalanced. Consequently, the average equatorial U–O bond distances of  $2.27 \text{ \AA}$ , and the approximately  $90^\circ$  O–U–O equatorial angles observed in the six-coordinate  $[\text{UO}_2(\text{HMPA})_4]^{2+}$  ground state [10] will increase to  $2.38\text{--}2.45 \text{ \AA}$  and decrease to approximately  $72^\circ$ , respectively, in the seven-coordinate  $[\text{UO}_2(\text{HMPA})_5]^{2+}$

transition state, by comparison with the equatorial bond distances and angles found in the seven-coordinate ground state  $[\text{UO}_2(\text{solvent})_5]^{2+}$  species [11, 12]. Space filling models based on crystal structure data show that, although the U–O bond making and bond breaking interactions accompanying solvent exchange are restricted to the equatorial plane, there is considerable freedom of movement for bond rotation of the  $-\text{P}(\text{NMe}_2)_3$  moieties of bound HMPA above and below the equatorial plane. Such movement may constitute a significant component of the observed  $\Delta V^\ddagger$ .

The  $\Delta V^\ddagger$  characterizing TMPA exchange on  $[\text{UO}_2(\text{TMPA})_5]^{2+}$  is very small and yet the exchange rate law indicates the operation of a D mechanism. The primary characteristic of a D process transition state is the elongation of the U–O bond of the leaving TMPA to the point at which there is no possibility of return. Simultaneously with this the other four U–O bond distances will decrease (possibly to as little as 2.27 Å), leading to a small  $\Delta V^\ddagger$  value, which also represents a very small fraction of, in this case, the partial molar volume of TMPA,  $V_s^\circ = 117.95 \text{ cm}^3 \text{ mol}^{-1}$ .

The exchange processes for both the  $[\text{UO}_2(\text{TMPA})_5]^{2+}$  and  $[\text{UO}_2(\text{HMPA})_4]^{2+}$  systems are characterized by negative activation entropies possibly an overall effect of shortening of the four U–O equatorial bonds (decrease in  $\Delta S^\ddagger$ ) and lengthening of one (increase in  $\Delta S^\ddagger$ ) in the  $[\text{UO}_2(\text{TMPA})_4]^{2+}$  transition state, and the opposite situation in the case of  $[\text{UO}_2(\text{HMPA})_5]^{2+}$  transition state.

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#### References

- 1 R. van Eldik and A. E. Merbach, *Comments Inorg. Chem.*, **12** (1992) 341.
- 2 A. E. Merbach, *Pure Appl. Chem.*, **54** (1982) 1479.
- 3 A. E. Merbach, *Pure Appl. Chem.*, **59** (1987) 161.
- 4 Y. Ducommun, P. J. Nichols and A. E. Merbach, *Inorg. Chem.*, **28** (1989) 2643.
- 5 C. Cossy and A. E. Merbach, *Pure Appl. Chem.*, **60** (1988) 1785.
- 6 C. Cossy, L. Helm and A. E. Merbach, *Inorg. Chem.*, **29** (1989) 2699.
- 7 D. Hugi-Cleary, L. Helm and A. E. Merbach, *J. Am. Chem. Soc.*, **109** (1987) 4444.
- 8 P.-A. Pittet, G. Elbaze, L. Helm and A. E. Merbach, *Inorg. Chem.*, **29** (1990) 1936.
- 9 D. L. Pisaniello, L. Helm, P. Meier and A. E. Merbach, *J. Am. Chem. Soc.*, **105** (1983) 4528.
- 10 L. R. Nassimbeni and A. L. Rodgers, *Cryst. Struct. Commun.*, **5** (1976) 301.
- 11 J. M. Harrowfield, D. L. Kepert, J. M. Patrick, A. H. White and S. F. Lincoln, *J. Chem. Soc., Dalton Trans.*, (1983) 393.
- 12 N. W. Alcock and S. Esperas, *J. Chem. Soc., Dalton Trans.*, (1977) 893.
- 13 G. J. Honan, S. F. Lincoln and E. H. Williams, *Inorg. Chem.*, **17** (1978) 1855.
- 14 J. Crea, R. Diguisto, S. F. Lincoln and E. H. Williams, *Inorg. Chem.*, **16** (1977) 2825.
- 15 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, New York, 3rd edn., 1988.
- 16 U. Frey, L. Helm and A. E. Merbach, *High-Pressure Res.*, **2** (1990) 237.
- 17 J. J. Depuech, J. Ducom and V. Michon, *Bull. Soc. Chim. Fr.*, (1971) 1848.
- 18 D. R. Stranks, *Pure Appl. Chem.*, **38** (1974) 303.