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## <sup>13</sup>C NMR Studies of the Chelate Ring Opening–Closing Process in (Nitrilotriacetato)vanadate(V) dioxovanadate(V) Ion

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Activation parameters of the exchange between two types of glycinate groups in (nitrilotriacetato)dioxovanadate(V) ion,  $[\text{VO}_2(\text{NTA})]^{2-}$ , have been determined as the results of <sup>13</sup>C NMR measurements over a range of temperatures between 277 and 306°K. The exchange mechanism is proposed on the basis of the chelate ring opening–closing process, assuming rupture of the metal–oxygen (glycinate) bond *trans* to V = O bond to give a five–coordinated intermediate.

### Introduction

Vanadium is widely recognized as a biologically important element.<sup>1,2</sup> The first two naturally occurring vanadium–proteins, V(V)–bromoperoxidase<sup>3,4</sup> and V–nitrogenase,<sup>5</sup> have been discovered recently.

The chemistry of vanadium(V) in aqueous solution is very complex, with the formation of various oligomeric forms as a function both of pH and of concentration.<sup>6</sup> Vanadium(V) forms stable complexes with a few ligands such as oxalate,<sup>7–10</sup> ethylenediaminetetraacetate (EDTA),<sup>11,12</sup> etc. The equilibrium and kinetic studies of some V(V)–aminopolycarboxylate complexes are reported.<sup>13–19</sup> The rarity of vanadium(V) complexes is mainly due to its strong oxidizing power, with most ligands being oxidized by the metal center.

NMR spectroscopy has been used extensively in the study of certain types of rapid equilibria. These must be processes involving the exchange of nuclei between different magnetic sites with first order rate constants falling in the range of approximately 1 to 10<sup>3</sup>s, in the temperature range (103 to 473°K) available within the probe of spectrometers. The associated free energies of activation for these processes may therefore range from 5 to 25 kcal/mol, and most of the studies which have been made deal with examples of two

general types of unimolecular processes.<sup>20,21</sup>

The first type involves changes of molecular geometry without major changes in bonding while the second type involves rapid bond reorganization in so-called fluxional molecules. The first type of process is for the most part restricted to conformational changes in organic molecules associated with rotation about single and double bonds, inversion of the conformation of cyclic compounds and of the configuration of certain trivalent atoms. The fluxional molecules have been particularly widely recognized in inorganic chemistry and organometallic chemistry, in addition quite a large number of organic compounds undergo electrocyclic bond reorganizations which are sufficiently fast to be studied by NMR lineshape methods.

In the previous study<sup>22</sup> we studied the solution structure of V(V)–nitrilotriacetate (NTA) complex ion,  $[\text{VO}_2(\text{NTA})]^{2-}$ , by <sup>13</sup>C NMR spectroscopy. The glycinate groups in the complex ion fall into two groups depending on whether or not they are *trans* to V = O bond but showed averaged signal at ambient temperature, indicating the occurrence of rapid exchange between two types of glycinate groups on NMR time scale. In this paper we have studied the exchange between two types of glycinate groups in (nitrilotriacetato)dioxovanadate(V) ion,  $[\text{VO}_2(\text{NTA})]^{2-}$ . From the <sup>13</sup>C NMR spectra over a range of temperatures we have obtained the kinetic data for the exchange by the total lineshape method.<sup>23</sup> And we have cal-

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culated the thermodynamic parameters of activation for the exchange system and proposed the exchange mechanism according to the chelate ring opening-closing process in  $[\text{VO}_2(\text{NTA})]^{2-}$  ion.

### Experimental

**Materials.** All reagent grade chemicals were used without further purification. Ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ), nitrilotriacetic acid, and deuterium oxide were purchased from Aldrich Chemical Company.

**Preparation of NMR Samples.** Sample solutions for  $^{13}\text{C}$  NMR measurements were prepared by dissolving the weighed amounts of  $\text{NH}_4\text{VO}_3$  and nitrilotriacetic acid in 20%  $\text{D}_2\text{O}$ /80%  $\text{H}_2\text{O}$  to provide a concentration of 0.250M complex ion. After dissolving the pH of the solution was adjusted to  $5.0 \pm 0.1$  with 50%  $\text{NaOH}$  or concentrated  $\text{H}_2\text{SO}_4$  solutions.

**Measurements of  $^{13}\text{C}$  NMR Spectra.**  $^{13}\text{C}$  NMR spectra of sample solutions were recorded on a Bruker AM-250 spectrometer at 62.896 MHz over a range of temperatures between 277 and 306 °K.  $^{13}\text{C}$  chemical shifts were measured relative to internal dioxane and referenced to DSS using the relation  $\delta_{\text{DSS}} = \delta_{\text{dioxane}} + 69.14$  ppm. The temperatures of the sample were measured on the spectrometer and were calibrated by inserting thermocouple into the sample tube. The samples were run in 10 mm tubes with broad band proton noise decoupling. A sweep width of 17857 Hz, an accumulation of 3000 transients with acquisition time of 0.918 s, and a pulse width of  $4\mu\text{s}$  corresponding to  $40^\circ$  flip angle were used.

**Evaluation of Rate Constants and Activation Parameters.** The total lineshape (TLS) equation of Gutowsky and Holm<sup>23</sup> for an uncoupled two-site exchange yields the rate constants by the comparison of experimental and calculated spectra. An IBM PC-AT computer is used to calculate the theoretical  $^{13}\text{C}$  NMR spectra. From the rate constants at a series of different temperatures the thermodynamic parameters of activation are calculated. The activation energy ( $E_a$ ) is obtained from the measurement of rate constants at a series of temperatures by fitting the data to the Arrhenius equation (1).

$$\log k = \log A - E_a/2.303RT \quad (1)$$

Values of  $E_a$  and the frequency factor ( $A$ ) were derived from linear plot of  $\log k$  vs.  $1/T$  by the least square method. The free energy ( $\Delta G^\ddagger$ ) of activation is computed from equation (2) based on the Eyring equation.

$$\Delta G^\ddagger = 4.57 \times 10^{-4} T [10.32 + \log(T/k)] \text{ kcal/mol} \quad (2)$$

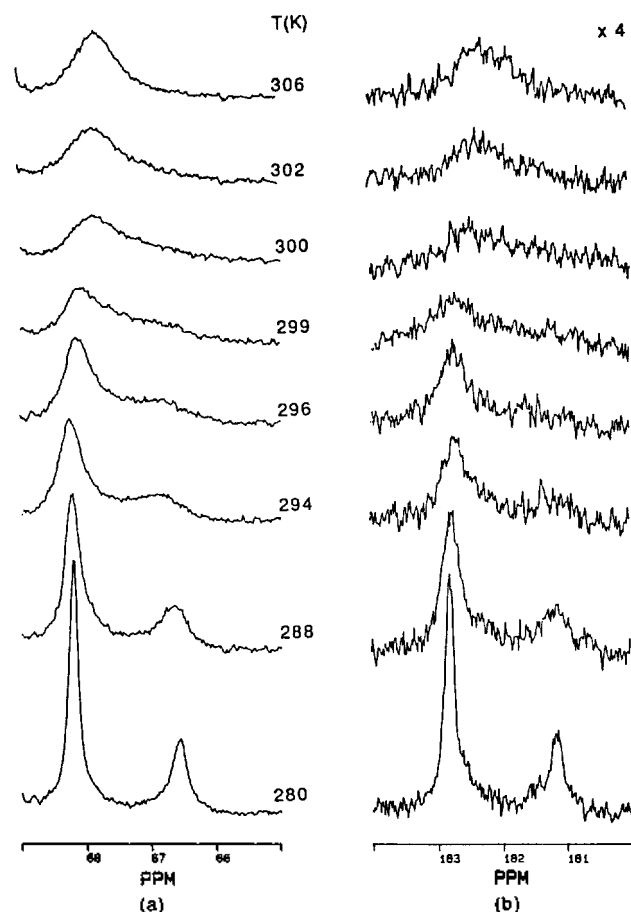
The enthalpy ( $\Delta H^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ) of activation are calculated by the usual equations, (3) and (4).

$$\Delta H^\ddagger = E_a - RT \quad (3)$$

$$\Delta S^\ddagger = (\Delta H^\ddagger - \Delta G^\ddagger)/T \quad (4)$$

### Results and Discussion

Nitrilotriacetic acid (NTA) can act as a quadridentate ligand to coordinate to vanadium (V), containing donor atoms of a nitrogen and three oxygens from three glycinate groups. It is supposed that the anion,  $[\text{VO}_2(\text{NTA})]^{2-}$ , might have a slightly



**Figure 1.** (a) Methylene and (b) carboxylate regions of the experimental  $^{13}\text{C}$  NMR spectra of  $[\text{VO}_2(\text{NTA})]^{2-}$  ion at various temperatures.

irregular octahedral geometry in which two double-bonded oxo ligands are *cis* to each other, similar to the structures of  $\text{V(V)}$ -oxalate<sup>7,8</sup> and  $\text{V(V)}$ -EDTA<sup>11,12</sup> complexes. There are three glycinate rings in the anion which are classified into two types of glycinate groups. Two glycinate groups are *cis* to and one glycinate is *trans* to the oxo ligand. The *trans* V-O (glycinate) bond might be significantly longer than *cis* V-O bond (glycinate), a good illustration of the structural *trans* effect. This  $\sigma$  bond strength weakening is reflected throughout the rest of the anion as the strongest of the inner C-O bonds are adjacent to the weaker of the V-O bonds. The terminal C=O bonds might be slightly shorter than the inner C-O bonds. The outer C=O bonds also fall into two groups, depending on *cis* and *trans* to V=O (oxo) bonds. The *trans* C=O bond might be longer than the *cis* C=O bond.

The experimental  $^{13}\text{C}$  NMR spectra of (nitrilotriacetato)-vanadate (V) ion,  $[\text{VO}_2(\text{NTA})]^{2-}$ , in aqueous solution at various temperatures are shown in Figure 1. Below the coalescence temperature ( $T_c$ ) of 300 °K two sets of resonance signals are observed, indicating that two types of glycinate groups exist in the anion. One (a glycinate) is resonated at 66.53 and 181.25 ppm and the other (two glycinate) is resonated at 68.23 and 182.90 ppm. But at higher temperatures the rate of exchange between two types of glycinate groups increases and two sets of signals coalesce to give a set of signals. The

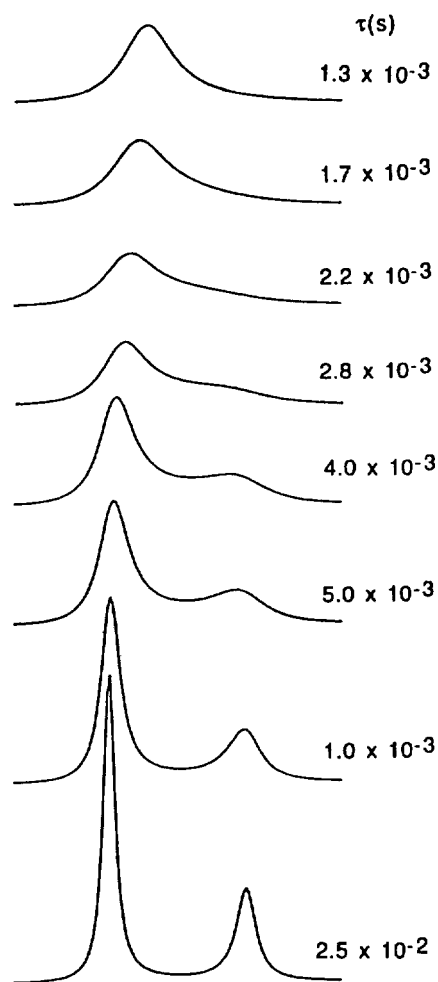


Figure 2. Calculated <sup>13</sup>C NMR spectra of the methylene groups in [VO<sub>2</sub>(NTA)]<sup>2-</sup> ion at various  $\tau$  values.

Table 1. Kinetic Data for the Exchange in [VO<sub>2</sub>(NTA)]<sup>2-</sup> ion

Temp (°K)	$\tau$ (s)	$k_A (= 0.66/\tau)(s^{-1})$	$\log k_A$
277	$5.0 \times 10^{-2}$	$1.3 \times 10$	1.12
280	$2.5 \times 10^{-2}$	$2.6 \times 10$	1.42
284	$1.5 \times 10^{-2}$	$4.4 \times 10$	1.64
288	$1.0 \times 10^{-2}$	$6.6 \times 10$	1.82
291	$7.0 \times 10^{-3}$	$9.4 \times 10$	1.97
294	$5.0 \times 10^{-3}$	$1.3 \times 10^2$	2.11
296	$4.0 \times 10^{-3}$	$1.7 \times 10^2$	2.23
299	$2.8 \times 10^{-3}$	$2.4 \times 10^2$	2.38
300 <sup>a</sup>	$2.2 \times 10^{-3}$	$3.0 \times 10^2$	2.48
302	$1.7 \times 10^{-3}$	$3.9 \times 10^2$	2.59
304	$1.6 \times 10^{-3}$	$4.1 \times 10^2$	2.62
306	$1.3 \times 10^{-3}$	$5.1 \times 10^2$	2.71

<sup>a</sup>Coalescence temperature.

calculated <sup>13</sup>C NMR spectra of methylene groups in the anion by the total lineshape (TLS) method<sup>23</sup> at various  $\tau$  values are shown in Figure 2. By comparing the experimental and calculated spectra we obtained the rate constants for the exchange as given in Table 1. We used only <sup>13</sup>C spectra of methylene group to compare the experimental and calculated

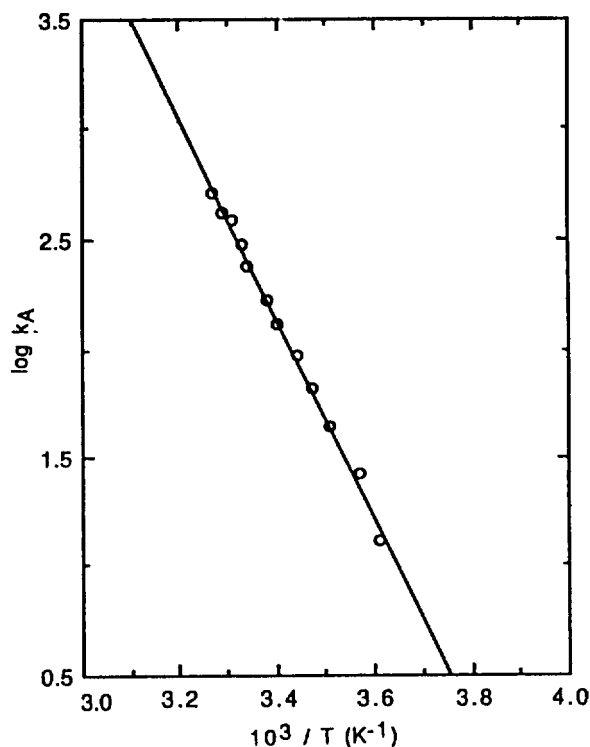


Figure 3. An Arrhenius plot of the kinetic data.

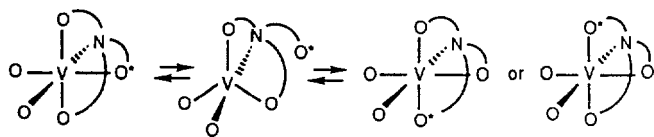
Table 2. Activation Parameters for the Exchange in [VO<sub>2</sub>(NTA)]<sup>2-</sup> ion

$E_a$ (kcal/mol)	$\log A$	$\Delta H^*_{300}$ (kcal/mol)	$\Delta S^*_{300}$ (eu)	$\Delta G^*_{300}$ (kcal/mol)
20.8	17.7	20.2	20.3	14.1

spectra because the experimental methylene group has the higher intensity of resonance signals. An Arrhenius plot of the kinetic data is shown in Figure 3 and gives the activation energy ( $E_a$ ), 20.8 kcal/mol, and the frequency factor ( $\log A$ ), 17.7. From these data other activation parameters were calculated and given in Table 2.

The large positive entropy of activation ( $\Delta S^*$ ) of 20.3 eu is reasonable for the chelate ring opening-closing of glycinate, so-called one-ended dissociation, reflecting the expected increase in freedom of the transition state. On the basis of a dissociation mechanism, it is plausible that the anion may have a trigonal bipyramidal intermediate which readily provide a path for exchange after first breaking of the metal-oxygen (glycinate) *trans* to V=O bond if metal-nitrogen bond has a longer life time. Next the free glycinate may attack a neighboring position, resulting the exchange of glycinate between *cis* to and *trans* to V=O. The high frequency factor ( $\log A$ ) of 17.7 suggests a greater charge separation in the transition state than in the ground state. On the basis of activation parameters obtained, we propose the exchange mechanism according to the chelate ring opening-closing process in [VO<sub>2</sub>(NTA)]<sup>2-</sup> ion as shown in Figure 4.

One might expect that  $\Delta S^*$  would be more positive for reactions accompanied by topological change than for a similar series of reactions that proceed with retention of confi-



**Figure 4.** Mechanism for the chelate ring opening-closing process in  $[\text{VO}_2(\text{NTA})]^{2-}$  ion.

guration.<sup>24,25</sup> The relationship means that the steric course is determined in the rate-determining step and this idea can be a dissociative type of mechanism. When the five-coordinated intermediate is trigonal bipyramidal, marked stereochemical change can be expected, leading to the positive  $\Delta S^\ddagger$  values. One-ended dissociation of the chelated glycinate group must be an important step in the chelate ring opening-closing process in the complex as in the several types of reactions of oxalato complexes.<sup>26</sup> V-O (glycinate) bond rupture to open the chelate ring is probably a rate-determining step as in the recemization of cobalt-oxalato complexes.<sup>27</sup>

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