ON THE PROPERTIES OF THE MULTIPLE BOND V = O IN VANADYL IONS

![Fig. 1](image)

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ON THE PROPERTIES OF THE MULTIPLE BOND V = O IN VANADYL IONS

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In the preceding paper (1) it was shown that, in aqueous solutions of vanadyl salts, the ratio of the proton magnetic-relaxation times T_1/T_2, and the time T_2 itself, are extremely sensitive to the state of the $V = O$ bond in VO^{2+} ions. Upon partial dissociation of this bond, caused by the action of acids or by the introduction of hydroxyl into the coordination sphere of VO^{2+}, a manyfold shortening of the time T_2 was observed and, correspondingly, an increase in the ratio T_1/T_2. Thus a comparatively simple and readily measurable characteristic was found—the relaxation of the solvent protons—which, using VO^{2+} ions as an example, makes it possible to begin studying in solutions the properties of complexes with multiple bonds. The importance of studying complexes with multiple bonds in the inner sphere was recently pointed out by G. B. Bokii (2). He also noted the desirability of detecting the states of a multiple bond by some less laborious method than can be done—when crystals are involved—by means of X-ray structural analysis. There are grounds for asserting that, for vanadyl solutions, such a route is provided by the method of nuclear magnetic relaxation.

Fig. 1

It seemed interesting to us, using the high sensitivity of the nuclear-relaxation method, to determine the influence of the isotopic composition of the solvent (water) on the $V = O$ bond. For this purpose, measurements were made of the proton relaxation times in freshly prepared equimolar solutions of $VOSO_4$ in ordinary water and in H_2O—D_2O mixtures. In Fig. 1, as an example, on the same time scale, oscillograms are shown of proton spin-echo signals obtained by means of a 90-180° sequence of radio-frequency pulses (3), for a 0.1 molar solution of $VOSO_4$ in H_2O (top) and in a mixture of 5% H_2O, 95% D_2O (bottom). The frequency of the oscillating magnetic field (ν_0) was 18.1 MHz. The experiments were carried out at $20^\circ C$. The distance between neighboring time marks is 2 msec. It is seen (Fig. 1) that the envelope of the echo signals in both cases is not uni-

Nakova. The following values of the transverse relaxation time of protons T_2 were found: for a 0.1-molar solution of $VOSO_4$ in H_2O, $T_2 = 11.7$ msec; and for a 0.1-molar solution of $VOSO_4$ in a mixture of 5% H_2O, 95% D_2O, $T_2 = 17.8$ msec. As ordinary water in the solvent is replaced by deuterium oxide, there is also a certain, but weaker, lengthening of the longitudinal relaxation time of protons (T_1), as a result of which the ratio T_1/T_2 decreases*. A summary of the values of the relaxation parameters of protons for 0.1-molar solutions of $VOSO_4$ in H_2O and in a mixture of 5% H_2O, 95% D_2O is presented in Table 1. Similar results were obtained also for 0.05-molar solutions of $VOSO_4$, which were half as concentrated.

Table 1

Relaxation parameters of protons for a 0.1-M solution of $VOSO_4$. $\nu_0 = 18.1$ Mc; $t \sim 20°$

	Solution in H_2O	Solution in a mixture of 5% H_2O, 95% D_2O (by volume)
T_1 (msec)	21.4	26.7
T_2 (msec)	11.7	17.8
T_1/T_2	~ 1.8	~ 1.5

Control experiments with aqueous solutions of Mn^{2+} and Cu^{2+} showed that partial replacement of ordinary water in the solvent by deuterium oxide (the maximum D_2O content was 95%) has absolutely no effect on the relaxation of protons in solutions of Mn^{2+} salts and only very weakly, almost within the limits of experimental error ($\sim 5\%$), shortens the relaxation time of protons (T_2) in solutions of Cu^{2+} salts**. Therefore, the observed influence of the isotopic composition of water on proton relaxation in solutions of vanadyl salts should be attributed to the specific molecular nature of the VO^{2+} ion. In accordance with the observed dependence between proton relaxation and the state of the intraionic bond $V = O$ (^{1}), it may be concluded that, when ordinary water in the solvent is replaced by deuterium oxide, the $V = O$ bond in vanadyl ions is strengthened. The following reasons are possible. Heavy-hydrogen water dissociates less readily than ordinary water, and at a lower concentration the hydrogen and hydroxyl ions must naturally act more weakly on the $V = O$ bond (cf. (^{1})). Further, heavy-hydrogen water, compared with ordinary water, dissolves mineral salts considerably less well; consequently, the solvation energy of cations in D_2O is probably less than in H_2O. This will enhance complex formation in the first of the solvents. Finally, a factor acting in the same direction is the difference in the zero-point vibrational energies of hydrated complexes of cations in ordinary and heavy-hydrogen water (^{6}).

Measurements were carried out with acidified solutions of $VOSO_4$. It was found that acidification of the solutions increases the dependence of the proton relaxation parameters on the isotopic composition of the water.

According to (^{7}), on heating aqueous solutions of VO^{2+}, the proton relaxation time T_2 is sharply shortened (by as much as an order of magnitude) and the ratio of the times T_1/T_2 increases, i.e., a change in the relaxation parameters is observed that is characteristic of partial dissociation of the $V = O$ bond (^{1}). Thus, the study of proton relaxation in solutions of vanadyl salts leads to the conclusion that the $V = O$ bond in VO^{2+} ions, despite its exceptional strength, cannot be regarded as an unchanging formation. This bond partially dissociates under the action of acids*** during hydrolysis and even with small increases in the temperature of the solutions*. Replacing ordinary water in the solvent by deuterium oxide decreases the polarization of the $V = O$ bond.

In conclusion we note that the results presented should be in a definite interrelation with the known facts concerning the nonconstancy (noncoincidence in different compounds) of the crystallographic distance $Me = X$ in the uranyl and certain other groupings with multiple bonds (^{9}, ^{10}).

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[*] Values of T_1 were measured by the "null" method (^{4}).

[**] The previously reported results of preliminary measurements of relative values of proton relaxation times T_1 in H_2O–D_2O mixtures containing paramagnetic ions (^{5}) were not confirmed on checking. Apparently, because of the always present slight nonlinearity of the measuring scheme (^{5}), it is unacceptable if the number of relaxing nuclei varies over wide limits.

[***] The protolytic reaction $VO^{2+} + H^+ \rightleftarrows VO \cdot H^{3+}$, which underlies the action of acids (^{1}), may play an important role in the mechanism of the vanadatometric method of oxidation-reduction titration (^{8}).

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* The maximum temperature to which the solutions were brought in work (7) was approximately 90°.

Note: Figure translations are in progress. See original paper for figures.

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