Inorganica Chimica Acta, 25 (1977) L43–L44

Rates of Oxygen Exchange between Vanadyl Ion (VO^{2+}) and Water

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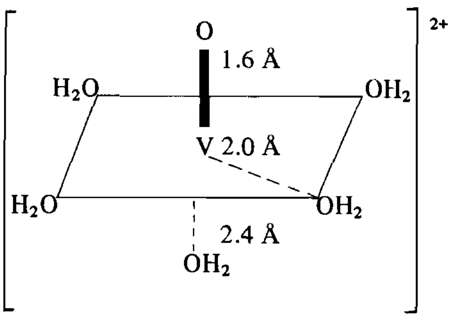
Received September 13, 1977

It is generally believed [1] that vanadium(IV) perchlorate in acidic aqueous solution exists in the form $[VO(OH_2)_5]^{2+}$. A unique feature of the ion is the multiple bond between V(IV) and one of the ligand oxygens giving a strong axial symmetry to the molecule. This results in three types of oxygens coordinated to a single positive ion center,



Experimental evidence for the equivalence of the four equatorial water molecules comes from X-ray data [2] and from esr studies [3].

The intrinsic rate at which these ligands exchange with solvent molecules is of fundamental interest from a mechanistic standpoint because of its close relationship to substitution reactions [4] on aqueous V(IV). Also, at least two other ions of this type appear to be important in aqueous chemistry, MoO^{3+} and CrO^{3+} but, because of enhanced hydrolysis tendencies, are much more difficult to study.

Definitive ^{17}O nmr studies have shown that the four [5–7] equatorial oxygens exchange with a rate constant of 5×10^2 sec^{-1} at 300 °K while the water *trans-* to the yl-oxygen has a residence time of about 10^{-11} seconds. It has been assumed that the yl-oxygen exchanges much more slowly, $k < 20$ sec^{-1}, but no direct rate measurements on it have yet been successful.

We now report measurements of the rate of isotopic oxygen exchange between the vanadyl oxygen, $VO^{2+}_{aq.}$, and water using two separation techniques which give equivalent results within the stated error limits.

Experimental

Vanadium(IV) perchlorate and chloride solutions were prepared from purified commercial $VOSO_4 \cdot 5H_2O$ by precipitation using the corresponding barium salts and were analyzed spectrally at 650 and 700 nm. The concentrated vanadium stock solutions were equilibrated for 20 days with ^{18}O enriched water and injected into large volumes of water of normal isotopic composition. The temperature of the reaction was maintained at 0 °C. At suitable time intervals during the exchange, vanadyl ion was precipitated from aliquotes or a portion of the solvent water was rapidly sampled by sublimation. These samples were analyzed for ^{18}O content by converting to $CO_2(K_3VOF_5)$ or equilibrating with $CO_2(H_2O)$ and measuring the 46/45 + 44 ratio of CO_2 with a Nuclide dual collector RMS mass spectrometer. The observed rate constant, k_{obs}, was evaluated from the least squares slopes of graphs of $\ln(N_\infty - N_0)/(N_\infty - N)$ *vs.* time.

A suitable precipitating agent for VO^{2+} was difficult to find, but we settled on a saturated, acidic solution of KHF_2. This allowed the use of dilute solutions of VO^{2+} but prevented the use of the perchlorate salt. While precipitation was rapid, some induced exchange was always present, ± 10%, but it was fairly reproducible providing V(V) was not present. Fluoride ion or HF appear to catalyze the VO_2^+–VO^{2+} electron exchange (and thus the ^{18}O exchange). Sampling by H_2O evaporation is intrinsically less precise because of fractionation effects and vapor–liquid nonequilibrium and requires much higher concentrations of VO^{2+} (especially since it contains only one oxygen) but is suitable for VO^{2+}–ClO_4^- solutions. In the initial studies, water samples were directly distilled from the main reaction mixture, while in later runs, small samples were removed and approximately 1/2 of the total water removed by sublimation. The former method gave higher precision due to the comparative lack of atmospheric contamination.

The stock solutions of VO^2–Cl^- were prepared essentially neutral. The pH of 50-fold diluted solutions was 2.2–2.9. The initial rate runs (by F^- precipitation) showed a half-time of about 30 minutes at 0 °C decreasing regularly to about 5 minutes with two days of aging of the stock solution. This suggested hydrolysis or oxidation of the stock solutions. With freshly prepared stock solutions the $t_{1/2}$ was 40–60 minutes. Reproducibility was about ± 25%. The addition of $Fe(NH_4)_2(SO_4)_2$ or $FeSO_4$ in trace amounts increased the half-time (Table I), to about 400 minutes (0 °C) and increased the reproducibility (± 10%). Since Fe^{2+} is known to reduce V(V) to V(IV), it is likely that its action is due to reduction of traces of V(V), preventing electron transfer and

TABLE I. VO^{2+}–H_2O Exchange.[a]

Sample Method	Data Points	Induced Exch. %	$10^2[Fe^{2+}]$	$10^5k(sec^{-1})$	$t_{1/2}$ min	*r*
F^- (prec.)	18	11%	0	28.6 ± 2.5	40.4	0.951
F^- (prec.)	6	8.7%	3.61	3.20 ± 0.24	361	0.989
H_2O (evap.)	5	0	3.56	2.60 ± 1.2	444	0.960
H_2O (evap.)	5	0	7.65	2.76 ± 0.29	418	0.989
H_2O (evap.)	6	0	18.7	3.25 ± 0.38	355	0.975
F^- (prec.)	6	12	3.70	2.98 ± 0.09	387	0.997
H_2O (evap.)	6	0	0	18.6 ± 1.4	62.2	0.989
H_2O (evap.)	7	0	0[b]	3.06 ± 0.22	377	0.995

[a] 0 °C, 0.1 *M* HCl, $[VOCl_2]$ = 0.223 *M*.

[b] 3.91×10^{-3} *M* $NH_2NH_2 \cdot 2HCl$ present.

lowering the resulting oxygen exchange rate. Partial confirmation of the explanation was obtained when hydrazine, which also reduces V(V) rapidly, gave the same slow rate constant. Within experimental error both sampling methods gave identical results in the presence of trace amounts of Fe^{2+} and $VOCl_2$. $VOSO_4$ and $VO(ClO_4)2$ showed no differences.

Results

Thus, the intrinsic rate constant of exchange, k_{obs}, between VO^{2+} and water at 0 °C is $2.98 \pm 0.25 \times 10^{-5}$ sec^{-1} ($t_{1/2}$ 388 min) as determined by F^- precipitation and by H_2O sampling [8]. The former showed about 10% induced exchange while the latter values were less precise. The rate constant was found to be independent of the $[Fe^{2+}]$ at 5×10^{-3} *M* or above, of the $[VO^{2+}]$ from 0.14–1.5 *M*, and of the particular stock solution used.

A series of experiments varying ionic conditions for $VOCl_2$ with 5×10^{-3} *M* $Fe(NH_4)_2(SO_4)_2$; 0.01 *M* HCl, 0.1 *M* HCl, 1.0 *M* HCl, 0.10 *M* H_2SO_4, 0.10 *M* $HClO_4$ and 0.1 *M* HCl + 5×10^{-3} *M* HF gave a constant value for k_{obs}. The average was 2.89 ± 0.26 $\times 10^{-5}$ sec^{-1} ($t_{1/2}$ 400 min). The rate of exchange is not sensitive to the nature of the anion and HF did not appreciably increase the rate constant.

The mechanism by which yl-oxygen exchange takes place is not known. A reasonable possibility for a low energy path would be a transition state in which the yl-oxygen and the water *trans* to it become equivalent through solvent proton transfer and V(IV) movement. If this were rapid enough (compared to the ^{18}O exchange rate), only two kinds of coordinated oxygen would appear (axial and equatorial) and the slow exchange of the yl-oxygen would not be observed. From the short residence time of the *trans*-water and the long residence time of the yl-oxygen, this is obviously not the case, suggesting that considerable energy is necessary to reach this symmetrical transition state.

Attempts are presently being made to increase the precision of the measurements in order to provide reliable activation parameters and also to investigate the VO_2^+–VO^{2+} electron exchange through V(V) catalysis which was observed.

Acknowledgment

We wish to express our appreciation to the Research Council of the University of Missouri for partial support of this work.

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8 Average of all values in 0.10 *M* HCl. ± value is average deviation from the mean. Incidentally, the overall isotopic change in the water samples is in agreement with 1.0 ± 0.1 oxygen exchanging per vanadium.