Metal-Ion Oxidations in Solution. Part III.[1] The Oxidation of 2-Mercaptosuccinic Acid by Vanadium(v)

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The oxidation of 2-mercaptosuccinic acid by the oxy-ions of vanadium(V) has been studied in the pH range 2·4—4·4 at temperatures from 0—25° with a stopped-flow technique. The reaction proceeds *via* the formation of a coloured intermediate complex followed by a slower electron-transfer step. The intermediate has a stability constant of ten and at 15° the observed rate constant for its formation may be expressed as $k_{obs} = [44·5 + 465(T)]$ sec.$^{-1}$ where T = 2-mercaptosuccinic acid. At the same temperature the rate constant for the redox process may be written as $k^1_{obs} = [5·0 + 40(T)]$ sec.$^{-1}$. The acid dissociation constants for 2-mercaptosuccinic acid have also been measured. Reaction of the intermediate leads to the formation of the disulphide, and a mechanism for the process is proposed. In the range studied, temperature has no significant effect on the rates.

KINETIC studies have been made of the oxidation of α-hydroxy-carboxylic acids by species such as cobalt(III) [1] and cerium(IV) ions [2,3] and the oxy-ions of manganese(VII),[4,5] chromium(VI),[6] and vanadium(V).[7,8] Further investigations include the reactions of α-mercapto-carboxylic acids which proceed at a much faster rate and which require special techniques, *e.g.*, a stopped-flow machine, to follow the kinetics. The oxidation of these α-thiols by cerium(IV) has recently been studied [9] and for a series of substituted α-mercaptans the energies and entropies of activation were similar. Here, we report the results of an investigation of the reaction between 2-mercaptosuccinic acid

[SH·CH(CO$_2$H)·CH$_2$·CO$_2$H = T] and the oxy-ions of vanadium(V).

It has been observed [10] that 2-mercaptosuccinic acid reduces vanadium(V) in acid media and several titri-metric procedures for the determination of 2-mercapto-succinic acid are based on its oxidation by other oxy-anions such as periodate, iodate, bromate, and chromate.[11,12] None of the analytical methods, however, are considered to be satisfactory since the extent of the reaction appears to depend on the alkalinity, temperature, and duration of the reaction.

EXPERIMENTAL

Kinetic Procedure.—The 2-mercaptosuccinic acid–vanadium(V) reactions were complete in less than a second but a coloured intermediate was formed which could be studied by means of the stopped-flow apparatus previously described.[9]

The reacting solutions were delivered rapidly and simultaneously from thermostatted syringes and feed lines into the mixing chamber, thence into a 'stop-flow' device *via* a 2 mm. (i.d.) quartz observation tube. Changes in intensity of monochromatic light passing across this

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[4] G. V. Bakore and R. Shanker, *Indian J. Chem.*, 1963, **1**, 108, 286, 331.
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[6] G. V. Bakore and S. Narain, *J. Chem. Soc.*, 1963, 3419.
[7] G. V. Bakore and R. Shanker, *Canad. J. Chem.*, 1966, **44**, 1717.

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[9] J. Hill and A. McAuley, *J. Chem. Soc. (A)*, 1968, 156.
[10] F. B. Martinez and M. del Carmen Meijon Mourino, *Inform. Quim. Anal. (Madrid)*, 1962, **16**, 91 (*Chem. Abs.*, 1964, **60**, 13,853a).
[11] F. Buscarons, J. Artigas, and C. Rodriguez-Roda, *Analyt. Chim. Acta*, 1960, **23**, 214.
[12] G. Aravamudan and C. Rama Rao, *Talanta*, 1963, **10**, 231.

tube at a point 1 cm. from the mixing chamber were detected by a photo-multiplier tube the output of which was fed to an oscilloscope which was triggered externally by means of a microswitch. Traces on the oscilloscope were photographed by means of a Polaroid camera.
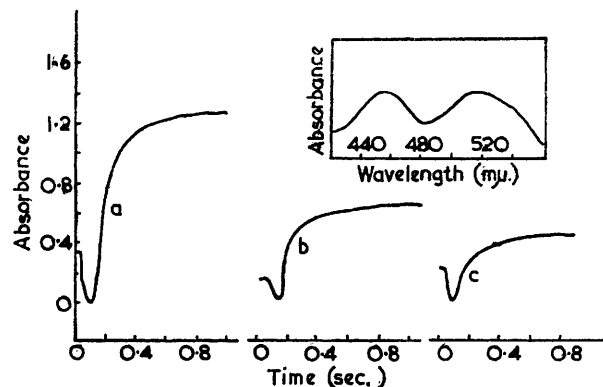

FIGURE 1   Oscillograph traces showing the formation and decomposition of the coloured intermediate species (spectral absorption curve shown as an inset); 10^{-3}M-NH_4VO_3 reacting with: a 5×10^{-2}, b 2.5×10^{-2}, and c 10^{-2} M-mercaptosuccinic acid

Millimolar solutions of AnalaR ammonium vanadate and (freshly prepared) 2-mercaptosuccinic acid were equilibrated for 30 min. at temperatures between 1 and 25° before being mixed in the apparatus. Typical traces obtained are shown in Figure 1. A faster time base than that shown was used to derive the rates of complex formation.

The concentration of the acid solutions was varied from 0·009 to 0·075M, the solid acid (Evans Chemetics Inc., N.Y., 99·7% pure) was used without recrystallisation. The pH of some solutions was varied within the range 2·4 to 4·4 by the addition of sodium hydroxide and the hydrogen-ion concentration of the solutions was measured before use by means of an E.I.L. pH meter.

The absorption spectrum of the purplish brown transient intermediate was determined by observing the change in absorbance of the reaction when the wavelength of incident light was varied (inset, Figure 1). All subsequent kinetic studies were made at 450 mμ since neither reactants nor final products absorbed at this wavelength.

All the experiments were conducted in the presence of an excess of 2-mercaptosuccinic acid to ensure that the reaction stopped at a stage corresponding to the formation of a disulphide. This approach also allowed the kinetic traces to be treated as pseudo-first order reactions and the 'apparent' first-order constants obtained from the $\log(a - x)$ vs. time, plots are shown in the Table. The values reported for the rate constants are the mean of at least four separate determinations.

Products.—Vanadate oxidation of 2-mercaptosuccinic acid followed by ether extraction gave white crystals which had an i.r. spectrum identical with a similar product from iodine oxidation which is known to give the disulphide.[13]

One mole of vanadate was found to react with 1.1 ± 0.1 moles of 2-mercaptosuccinic acid as shown by back titration of the 2-mercaptosuccinic acid which remained after treatment with differing amounts of vanadium(v).

On the addition of the vanadate solution to the mercaptosuccinic acid the characteristic blue colour of vanadium(IV)

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Apparent rate constants for the formation and dissociation of the intermediate complex at 15·3° *

Total acid concentration ($\times 10^2$M)	pH	Apparent rate constants (sec.$^{-1}$) †	
		k' Formation [a]	k'' Decomposition [b]
5·0	2·42	70	6·9
5·0	2·62	61	6·5
5·0	3·12	59	6·3
5·0	3·31	53	6·0
5·0	3·55	56	5·6
5·0	3·80	55	5·4
5·0	4·3	—	5·0
5·0	4·4	49	4·7
1·0	2·62	43	—
1·5	2·58	41	5·4
2·0	2·52	51	5·3
2·5	2·50	51	5·7
3·0	2·48	57	5·6
5·0	2·42	59	6·8
7·0	2·39	69	7·5

* No systematic change in k values was observed on variation of temperature between 2·1° and 25·2°.   † The mean of at least four determinations. Mean deviations: [a] $\pm 10\%$, [b] $\pm 4\%$.

species appeared and the pH of the solution increased. Potentiometric titrations such as those recorded in Figure 2 indicated that the pH change caused by the addition of a mmole of vanadate was equivalent to the change produced by 2 ± 0.3 mmoles of sodium hydroxide.
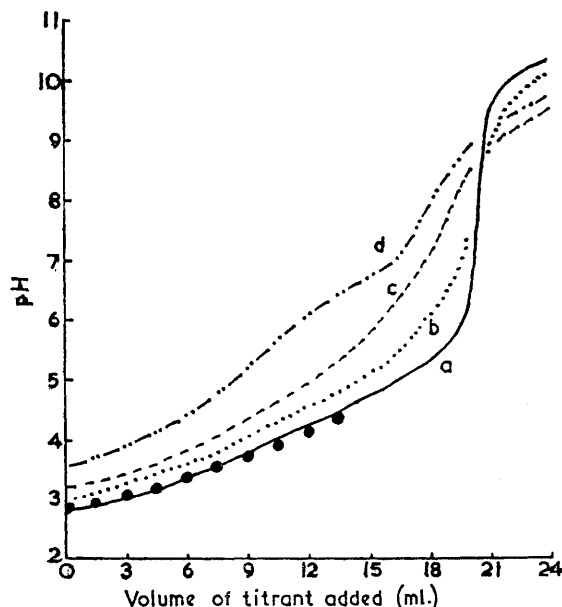

FIGURE 2   Potentiometric titration of 0·02M-mercaptosuccinic acid (25 ml.) by 0·05M-sodium hydroxide, after the addition of a 0, b 5 ml., c 10 ml., and d 20 ml. of 0·01M-ammonium vanadate solution. The points (●) represent the pH changes observed on titration of 0·02M-mercaptosuccinic acid with 0·025M-ammonium vanadate

Only part of this pH change can be attributed to the reactions in which the added ammonium tetravanadate is converted to species such as VO_2^+, $[H_2V_{10}O_{28}]^{4-}$, and $[HV_{10}O_{28}]^{5-}$ these being the predominant species of vanadium(v) in acid media. Calculations based on equilibrium data [14] indicate that the amount of VO_2^+ present decreases from over 70% of the total at pH 2·4 to about 1% at pH 4·4. This change in the relative proportions of the vanadium(v) species with pH did not appear to influence the

kinetics significantly, so that the interconversion of the vanadium(v) species is considered to occur with the time of mixing of the solutions. With solutions of fixed pH (*i.e.*, fixed proportion of vanadium species) the observed rate constants were found to vary with the concentration of un-ionised acid in exactly the same way as when the concentration of un-ionised acid was varied through pH changes (cf. Figures 3 and 4).
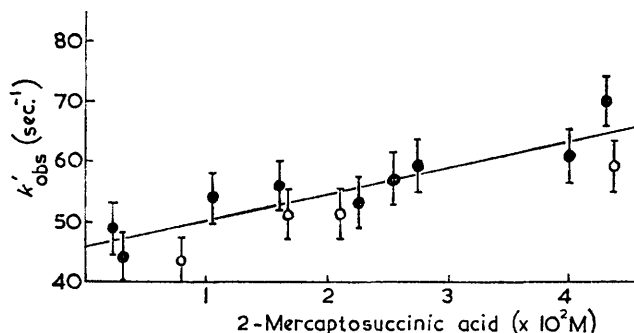

FIGURE 3 Variation in apparent rate constant with un-ionised mercaptosuccinic acid concentration for formation reaction at 15·3° with 10^{-3}M-vanadate solution ($\bullet$, $(TMA)_T = 0·05$M, pH varied; $\bigcirc$, $(TMA)_T$ varied)
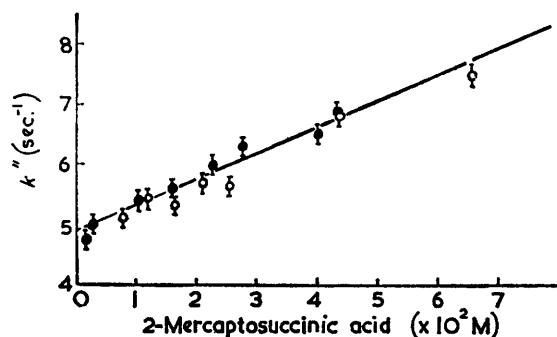

FIGURE 4 Variation in apparent rate constant with un-ionised mercaptosuccinic acid concentration, for redox reaction at 15·3°, with 10^{-3}M-vanadate solution ($\bullet$, $(TMA)_T = 0·05$M, pH varied; $\bigcirc$, $(TMA)_T$ varied)

RESULTS AND DISCUSSION

The oscilloscope traces (cf. Figure 1) can be regarded as being composed of two segments. After the flow stopped, the initial fall in the curve was attributed to the formation of the coloured intermediate. Since an excess of 2-mercaptosuccinic acid was present, this section was treated mathematically as a first-order reaction, the absorbance at the minimum being taken as a measure of the concentration of the complex at equilibrium $[(VT)_{eq}$, time t_e. Preceding absorbances represented complex concentrations (VT) at various time t. Log $[VT)_{eq} - (VT)]$ was plotted against $(t_e - t)$ to yield the first-order constants recorded in Table 1. The subsequent rise in the trace recorded the decomposition of the intermediate complex, the absorbance at time t_d $(t_d > t_e)$ being directly related to the concentration of the complex remaining $(VT)_d$. First-

order constants were calculated from the slope of log $[(VT)_{eq} - (VT)_d]$ *vs.* $(t_d - t_e)$ plots.

As shown in Table 1, the first-order rate constants calculated from the oscilloscope traces varied in magnitude with the pH of the solution and with the total concentration of acid present. Linear relationships were observed, however, when the rate constants were plotted against the concentration of undissociated acid present, as shown in Figures 3 and 4.

The acid dissociation constants for 2-mercaptosuccinic acid were determined from a pH-titration curve (Figure 2) to give values of 3·2 and 4·7 for pK_1 and pK_2 respectively. These values were used to calculate the concentration of undissociated acid present in the reactant solutions.

The absorbance of the kinetic traces decreased with decreasing 2-mercaptosuccinic acid concentration and suggested a preliminary equilibrium step prior to the electron-transfer reaction (Figure 1). The existence of such equilibria have been postulated previously from kinetic data [15-17] but only on few occasions has physical evidence for the existence of these intermediates been established.[18,19]

The rates of formation of the initial complex were so fast that measurement was just within the range of the machine. Accordingly, the results are of limited precision, about $\pm 10\%$ variation. The plot shown in Figure 3 is considered, however, to be valid and it has been used to estimate an equilibrium constant for the formation of the coloured intermediate.

As shown in Figure 1, the intensity of the colour increased as the concentration of 2-mercaptosuccinic acid present was increased, and the reaction is considered to involve the equilibrium
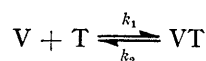
$$V + T \underset{k_2}{\overset{k_1}{\rightleftharpoons}} VT$$

where V represents a vanadium(v) species and T represents the 2-mercaptosuccinic acid molecule.

With T in large excess it is easily shown that

$$d(VT)/dt = [(VT)_{eq} - (VT)][k_2 + k_1(T)]$$

Since pseudo-first-order reaction conditions prevailed the apparent rate constant for formation (k^1) equals $[k_2 + k_1(T)_{eq}]$. The plot of k^1 against $(T)_{eq}$ as shown in Figure 3 accordingly has a slope of k_1 and intercept equal to k_2. From the graph $k_1 = 465 \pm 50$ mole^{-1} l. sec.$^{-1}$ and k_2 equals $44·5 \pm 3$ sec.$^{-1}$, which yields a value of K (*i.e.*, k_1/k_2) of 10·5. Variations in the magnitude of the absorbance as shown in Figure 1 are consistent with an equilibrium constant of this order.

This derivation assumes that decomposition (k'') is considerably slower than formation, an assumption which is justified by the difference in magnitude of the two rates (see below).

From Figure 4 it is seen that the rate constant for

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[16] A. A. Clifford and W. A. Waters, *J. Chem. Soc.*, 1965, 2796.
[17] N. Sutin, *Ann. Rev. Phys. Chem.*, 1966, **17**, 153.

[18] T. J. Connocchioli, G. H. Nancollas, N. Sutin, *Inorg. Chem.*, 1966, **5**, 1.
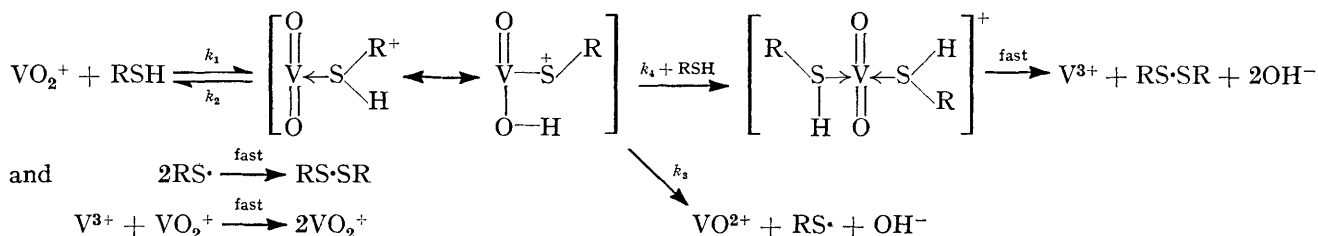[19] J. Hill, A. McAuley, and W. F. Pickering, *Chem. Comm.*, 1967, 573.

the decomposition of the intermediate complex, k'', may be expressed in the form $k'' = k_3 + k_4(T)$, a binary relationship suggesting two electron-transfer paths, one of which involves the reaction of the complex with a second mole of undissociated acid. At 15°, k'', may be represented by the relationship $[5 + 40(T)]$ sec.$^{-1}$.

A change in temperature from 1 to 25° had no significant effect on the magnitude of the apparent rate constants (cf. Table) hence it must be concluded that either the reaction has a very small activation energy or that there are compensating temperature effects within the overall processes.

The interpretation of the pH effect on the rate in terms of its effect on the concentration of uncharged acid molecules seems justified, since in this way two different sets of data can be correlated in a single plot (Figures 3 and 4).

In addition, it is reasonable to predict that less energy would be required to displace hydrogen from the thiol group if the latter is present in an uncharged molecule.

pH Measurements indicated that more than 1 mole of base was produced when the vanadium(v) reacted with the thiol. If 2-mercaptosuccinic acid is written as RSH, a mechanism which is consistent with the experimental observations may be represented as follows:

from the intercept in Figure 4 is $5 \cdot 0 \pm 0 \cdot 2$ sec.$^{-1}$ whilst the slope yields $k_4 = 40 \pm 3$ mole^{-1} l. sec.$^{-1}$.

The potentiometric titrations indicated no significant complex formation between vanadium(iv) species and 2-mercaptosuccinic acid species at pH values less than 6 and there was no evidence for species of the type VO(OH)SR analogous to the compound VO(OH)SH isolated after reduction of ammonium vanadate by hydrogen sulphide.[20]

Although hydrogen sulphide reduces vanadium(v) to vanadium(iv), ammonium sulphide is reported [21] to react with neutral or alkaline vanadate solutions to give brown or purple-red thiovanadate solutions which yield violet crystals of $(NH_4)_3VS_4$ on evaporation. Freshly prepared solutions of this ammonium thiovanadate change colour (from purple to brown) and this is attributed to hydrolysis leading to the formation of species such as $NH_4(VS_3H_2O)$.

Because of this hydrolysis, it has not been possible to clearly characterise the absorption spectrum of the purplish-brown thiovanadate solutions, but there is distinct absorption between 420 and 550 mμ which cannot be attributed to either ammonium vanadate or ammonium sulphide. This broad band corresponds to the region of maximum absorption observed in the 2-mercaptosuccinic acid–vanadate reaction (inset, Figure

That vanadium can act as a two-electron oxidant in its reaction with α-hydroxycarboxylic acids has been established previously.[7,8] The value of k_3 obtained

1) and it tends to confirm that the transient intermediate is a vanadium(v)–sulphur species.

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[21] P. Spacu and C. Gheorghui, *Acad. Rep. Populare Rome, Studii Cercetari Chim.*, 1958, **6**, 619 (*Chem. Abs.*, 1959, **53**, 14,813f).