154. *Oxidations of Organic Compounds with Quinquevalent Vanadium. Part IX.*[1] *Bromide-catalysis of Some Reactions.*

By K. Julian and William A. Waters.

Hydrogen bromide catalyses the oxidations of both cyclohexanol and propan-2-ol by acid solutions of vanadium(v); there is a similar catalysis of the oxidative bromination of crotonic and cumene-*p*-sulphonic acid. Relevant kinetic data are reported. A substrate-independent rate, identical for all four compounds, is thought to be due to the forward reaction:

$$\mathrm{V(OH)_2Br_2^+ + Br^- \longrightarrow V^{IV}(OH)_2Br^+ + Br_2^-}$$

This yields the reactive bromine radical-ion $(\cdot\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}-\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}:)^-$.

With propan-2-ol and crotonic acid a slower reaction is also ascribed to oxidation by the ion $\mathrm{V(OH)_2Br^{2+}}$.

We have found that though acid solutions of vanadium(v) do not oxidise maleic acid or convert it into fumaric acid this isomerisation is rapid when a small amount of an inorganic bromide is also added. Since bromine atoms are immediate catalysts of the isomerisation of maleic to fumaric acid[2] this observation indicates a rapid reaction:

$$(1) \quad \mathrm{V^V + Br^- \longrightarrow V^{IV} + Br\cdot}$$

and it was envisaged that traces of bromine atoms generated in this way might catalyse a number of other homolytic reactions of vanadium(v). This is indeed the case for oxidation of alcohols and cumene-*p*-sulphonic acid, and for the oxidative bromination of crotonic acid. Since this work began similar bromide-catalysed reactions of cerium(IV) have been reported by Langkammerer, Jenner, Coffmann, and Howk.[3]

It has been shown by Bobtelsky and Czosnek[4] that the reaction

$$(2) \quad \mathrm{2V^V + 2Br^- \longrightarrow 2V^{IV} + Br_2}$$

is slow and reversible unless bromine is removed from the mixture as it is formed. We find that in the presence of an oxidisable organic substrate reduction of vanadium(v) is an irreversible first-order reaction. Fig. 1 shows the dependence of the rate of reduction of vanadium(v) on the substrate concentration for cyclohexanol, crotonic acid, and cumene-*p*-sulphonic acid in the presence of bromide anions, and Fig. 2 shows similar data for propan-2-ol. It can be seen that in the presence of bromide an identical reaction, of zero order with respect to the organic substrate, is imposed on a first-order reaction. In the case of cyclohexanol this first-order reaction is the direct oxidation of the alcohol by vanadium(v) which has been studied by Littler and Waters,[5] but with both propan-2-ol and crotonic acid there is also a slow first-order reaction that does not occur in the absence of bromide. Too much reliance cannot be placed on the results for cumene-*p*-sulphonic acid since it yields transient free radicals which are easily autoxidised, and certain of the figures for propan-2-ol are slightly suspect for the same reason (see Fig. 2), but it has been checked that autoxidation does not intervene as a secondary reaction with the other two substrates.

All our kinetic studies have been carried out in perchloric acid solutions since the perchlorate anion does not form vanadium complexes which might complicate the kinetic picture.

For cyclohexanol we have checked that the direct oxidation rate, at the same acidity,

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[1] Part VIII, Jones and Waters, *J.*, 1961, 4757.

[2] Derbyshire and Waters, *Trans. Faraday Soc.*, 1949, **45**, 749.

[3] Langkammerer, Jenner, Coffmann, and Howk, *J. Amer. Chem. Soc.*, 1960, **82**, 1395.

[4] Bobtelsky and Czosnek, *Z. anorg. Chem.*, 1932, **205**, 401.

[5] Littler and Waters, *J.*, 1959, 4046.

by Br_3^- ions (*i.e.*, molecular bromine in an excess of hydrogen bromide) is much slower than the catalysed rate shown in Fig. 1.

Our observations therefore accord with the view that a reaction of the general type of equation (1) is followed by rapid reactions such as (3—5):

(3) $R_2CH{\cdot}OH + Br{\cdot} \longrightarrow R_2C(OH){\cdot} + Br^-$

(4) $C{=}C + Br{\cdot} \longrightarrow C{-}CBr{\cdot}$

(5) $HO_3S{\cdot}C_6H_4{\cdot}CHMe_2 + Br{\cdot} \longrightarrow HO_3S{\cdot}C_6H_4{\cdot}CMe_2{\cdot} + Br^-$

giving organic radicals which are then oxidised immediately by vanadium(v), and that with both crotonic acid and propan-2-ol another, slower, bromide-catalysed reaction must also be involved.

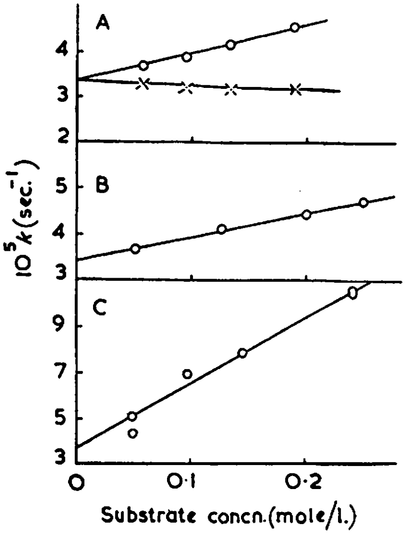

FIG. 1.

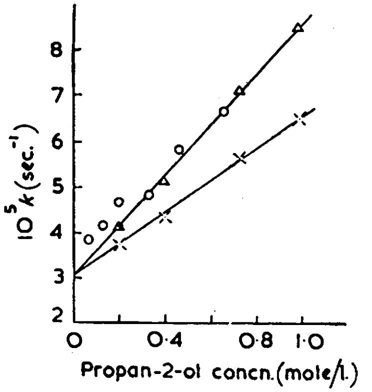

FIG. 2.

FIG. 1. Dependence on organic substrate concentration of the rate of oxidation by vanadium(v) in the presence of bromide on the concentration of organic substrate.

(A) Cyclohexanol. Initial $[V^V] = 0{\cdot}049$M. Initial $[Br^-] = 0{\cdot}16$M. $[H_3O^+] = 2{\cdot}90$M. Ionic strength = 3M.

○, Measured rate constant. ×, Rate constant due to bromide catalysis [by subtraction of the rate constant due to the direct vanadium(v)–cyclohexanol reaction].

(B) Crotonic acid. Initial $[V^V] = 0{\cdot}0445$M. Initial $[Br^-] = 0{\cdot}16$M. $[H_3O^+] = 2{\cdot}91$M. Ionic strength = 3M. There is no reduction of vanadium(v) in the absence of bromide.

(C) Cumene-*p*-sulphonic acid (approximate data). Initial $[V^V] = 0{\cdot}044$M. Initial $[Br^-] = 0{\cdot}16$M. $[H_3O^+] = 3{\cdot}15$M. Ionic strength = 3·24M. The change in cumene-*p*-sulphonic acid concentration was compensated by means of a sulphuric acid solution of equivalent strength.

FIG. 2. Dependence on propan-2-ol concentration of its rate of oxidation by vanadium(v) in the presence of bromide.

Δ, Measured rate constant in air. ×, Rate constant in air due to bromide catalysis [by subtraction of the rate constant due to the direct vanadium(v)–propan-2-ol reaction in air]. Initial $[V^V] = 0{\cdot}047$M. Initial $[Br^-] = 0{\cdot}16$M. $[H_3O^+] = 2{\cdot}90$M. Ionic strength = 3M.

○, Measured rate constant in nitrogen. Initial $[V^V] = 0{\cdot}0455$M. Initial $[Br^-] = 0{\cdot}16$M. $[H_3O^+] = 2{\cdot}9$M. Ionic strength = 3M.

To elucidate the mechanisms more clearly further kinetic work has been carried out with cyclohexanol and crotonic acid. Fig. 3 shows that for cyclohexanol the catalytic effect of bromide is of the third order with respect to $[Br^-]$; Fig. 4 shows that for both substrates the rapid reaction has an order of about 2·2 with regard to the Hammett acidity function h_0. The values of the logarithmic Hammett function H_0 used in Fig. 4 are those of Paul and Long [6] for perchloric acid solutions of 6M-ionic strength, and as shown previously [7] are reasonable values for 5M-solutions also. To accord both with these observations and with the fact that the oxidation of bromide by vanadium(v) is reversible we suggest that the following equilibria are rapidly attained:

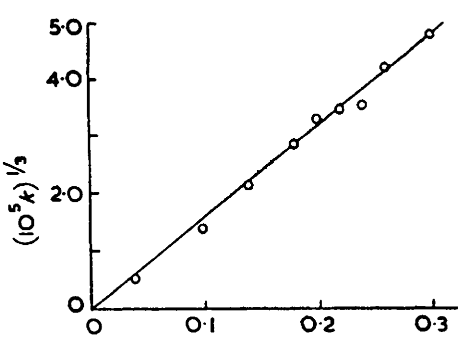

FIG. 3.

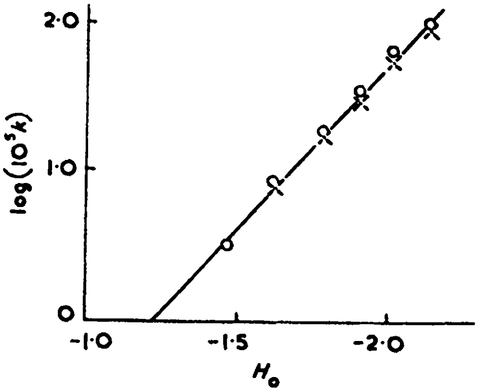

FIG. 4.

FIG. 3. Third-order dependence on bromide concentration of the rate of oxidation of cyclohexanol.

Initial $[V^V]$ = 0·445M. [Cyclohexanol] = 0·097M. $[H_3O^+]$ = 1·91M. Ionic strength = 5M. The plotted values of k are those of the bromide-catalysed reaction [obtained by subtraction of those of the direct vanadium(v)–cyclohexanol reaction].

FIG. 4. Dependence of the rate of oxidation on the Hammett acidity function.

×, Crotonic acid. Initial $[V^V]$ = 0·045M. Initial $[Br^-]$ = 0·16M. [Crotonic acid] = 0·1M. Ionic strength = 5M.

○, Cyclohexanol. The plotted values of k are those due to the bromide-catalysed reaction [obtained by subtraction of the direct vanadium(v)–cyclohexanol reaction]. Initial $[V^V]$ = 0·0445M. Initial $[Br^-]$ = 0·16M. [Cyclohexanol] = 0·097M. Ionic strength = 5M.

$$(6)\quad VO_2^+ + H_3O^+ \rightleftharpoons V(OH)_3^{2+} \qquad (K_6)$$

$$(7)\quad V(OH)_2^{2+} + Br^- \rightleftharpoons V(OH)_3Br^+ \qquad (K_7)$$

$$(8)\quad V(OH)_3Br^+ + H^+ \rightleftharpoons V(OH)_2Br^{2+} + H_2O \qquad (K_8)$$

$$(9)\quad V(OH)_2Br^{2+} + Br^- \rightleftharpoons V(OH)_2Br_2^+ \qquad (K_9)$$

From the above it is evident that

$$[V(OH)_2Br_2^+] = K_6K_7K_8K_9[VO_2^+][Br^-]^2[H^+]^2$$

Following this, the rate-determining reaction could well be:

$$(10)\quad V(OH)_2Br_2^+ + Br^- \overset{\text{Slow}}{\rightleftharpoons} V^{IV}(OH)_2Br^+ + Br_2^-$$

which again must be reversible to accord with the observations of Bobtelsky and Czosnek,

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[6] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

[7] Jones and Waters, *J.*, 1961, 630.

though under our conditions the radical-ion Br_2^- will be removed rapidly by the organic substrates. Consequently

$$-d[V^V]/dt = k_{10}K_{6-9}[VO_2^+][Br^-]^3[H^+]^2$$

Though a water molecule is involved in the transition state of reaction (6), one is eliminated in reaction (8), and so the acidity dependence would be expected to follow the trend of a Hammett acidity function dependence rather a proton concentration dependence.

Since there is good reason [5] to conclude that the direct oxidation of alcohols by the ion $V(OH)_3^{2+}$ proceeds through a 4-co-ordinated complex $R\text{-}\underset{H}{O}\rightarrow V(OH)_3^{2+}$ we suggest that the second new species that reacts with propan-2-ol, and probably with crotonic acid, is the ion $V(OH)_2Br^{2+}$.

Product studies with crotonic acid showed that a complex mixture had been produced, αβ-dibromobutyric acid being the major component. The formation of a trace of γ-bromocrotonic acid was suspected because the total product was a skin-irritant, but attempts at identification of minor products were not successful.

A few experiments have been carried out to explore the possibility that chloride anions would have a similar catalytic effect. In concentrated (3·9M-)hydrochloric acid vanadium(V) does attack crotonic acid slightly and in non-aqueous solutions vanadium oxychloride, $VOCl_3$, does attack olefins, but the acceleration of the rate of oxidation of alcohols is very slight.

EXPERIMENTAL

Materials.—Vanadium(V) solutions in perchloric acid were prepared as described in Part II.[8] Hopkin and Williams's "recrystallised grade" sodium perchlorate was used to maintain constant ionic strengths, and Harrington's "laboratory chemical" hydrobromic acid was used as the source of bromide. Cyclohexanol and propan-2-ol were purified until ketone-free. Crotonic acid, m. p. 72°, was repeatedly crystallised from water until it had no direct action on acidic vanadium(V) solutions. A solution of cumene-*p*-sulphonic acid was prepared by sulphonating cumene, separating the calcium salt of the sulphonic acid, and passing a solution of the latter through a column of Amberlite resin IR-120 (H^+).

Product Studies of the Reaction with Crotonic Acid.—Continuous extraction of an oxidised mixture from crotonic acid (30 g.) gave a yellow solution which on concentration deposited αβ-dibromobutyric acid (42·5 g.), m. p. 88° (from water) (Found: C, 20·0; H, 2·4; Br, 65·0. Calc. for $C_4H_6Br_2O_2$: C, 19·5; H, 2·4; Br, 65·0%). The residual solution on evaporation gave a pale yellow oil (3·0 g.). Esterification of this with methanol and sulphuric, followed by vapour-phase chromatography, showed two esters other than methyl dibromobutyrate to be present in small amounts, but distinct separation of this ester from 10% of its weight of authentic methyl γ-bromocrotonate could not be effected.

Kinetic Measurements.—These were carried out at 49·9° ± 0·1° as described in Part II.[8] Reactions such as (2), which do not involve the organic substrate, have no effect on the oxidising capacities of reacting mixtures.

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[8] Littler and Waters, *J.*, 1959, 3014.