254. *Oxidations of Organic Compounds with Quinquevalent Vanadium. Part I. General Survey; and the Oxidation of Pinacol.*

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The susceptibility of organic compounds to oxidation by quinquevalent vanadium in sulphuric acid solution has been qualitatively surveyed. Evidence of induced polymerisation of acrylonitrile and of reduction of mercuric chloride indicates that a free-radical mechanism operates in most or all such oxidations, vanadium(V) only being reduced to vanadium(IV). The oxidation of pinacol has been studied kinetically, with a volumetric method for estimating vanadium(V). The reaction is of first-order in vanadium(V) and in pinacol, but the dependence on acidity is complex, *i.e.*, $-d[V^V]/dt = k_0[\text{Pinacol}][V^V](1 + f[H^+])$, and there is a small linear salt effect. Acrylonitrile, oxygen, and iron(III) have no significant effect on the rate of oxidation.

THE study of the mechanisms of oxidation of organic compounds by quinquevalent vanadium has, besides its own interest, implications about the behaviour of vanadium oxide catalysts, and is of value in problems concerning possible actions of transient ions of chromium and manganese that may be concerned in certain oxidations by both chromic acid and potassium permanganate.[1] The subject was cursorily surveyed by Morette and Gaudefroy [2] primarily from an analytical viewpoint; but kinetic investigation has not extended beyond Bobtelsky and Glasner's study of oxidations of oxalic acid, formaldehyde, and ethanol.[3]

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[1] W. A. Waters, *Quart. Rev.*, 1958, **12**, 277.

[2] Morette and Gaudefroy, *Bull. Soc. chim. France*, 1954, 956.

[3] Bobtelsky and Glasner, *J. Amer. Chem. Soc.*, 1942, **64**, 1462.

TABLE 1.

Substrate	Oxidation test	Polymerisation test	Mercuric chloride test
Acids			
Formic	O	—	—
Acetic	O	—	—
Succinic	O	—	—
Malonic	M	—	—
Ethylmalonic	M	C	—
Diethylmalonic	O	—	—
Phenylacetic	SS	S	—
Oxalic	S	SS	O
Crotonic	O	—	—
Hex-2-enoic	M	S	—
Fumaric	O	—	—
Maleic	SS	S	SS
Lactic	F	S	SS
Glycollic	F	S	—
Tartaric	F	S	A
β-Hydroxybutyric	MB	S	—
Pyruvic	FF	SS	S
Glycine, leucine	O[SS]	—	—
Aldehydes			
Formaldehyde	S	S	A
Acetaldehyde	FB	S	—
Chloral (hydrate)	O[SS]	—	—
Propaldehyde	F	C	A
Butyraldehyde	F	C	C
Crotonaldehyde	F	C(G)	—
Ketones			
Acetone	M	C	S
Ethyl methyl ketone	F	S	S
Diethyl ketone	F	S	SS
Di*iso*propyl ketone	F	S	—
*cyclo*Pentanone	F	S	C
*cyclo*Hexanone	FD	C	—
Methyl*cyclo*hexanone	M	C	—
*cyclo*Heptanone	SD	C	—
Acetonylacetone	F	C	—
Diacetyl	FF	C	A
Alcohols			
Methanol	SB	C	SS
Ethanol	SB	C	—
Butan-1-ol	SB	C	—
Propan-2-ol	SB	C	—
*cyclo*Hexanol	SB	S	—
tert.-Butyl alcohol	OB[OB]H	—	—
Benzyl alcohol	SB	—	—
Ethylene glycol	SB	S	SS
1 : 2-Butylene glycol	FB	S	—
2 : 3-Butylene glycol	F	C	—
Pinacol	F	C	C
*cis-cyclo*Hexane-1 : 2-diol	FB	C	—

Substrate	Oxidation test	Polymerisation test	Mercuric chloride test
Alcohols			
*trans-cyclo*Hexane-1 : 2-diol	FB	C	—
1 : 2-Dimethyl*cyclo*hexane-*trans*-1 : 2-diol	F	S	—
1 : 2-Dimethyl*cyclo*pentane-*trans*-1 : 2-diol	F	C	—
Glycerol	FB	S	S
Sorbitol	FB	S	—
Mannitol	MB	C	SS
Methyl α-D-glucoside	SB	SS	—
Methyl α-D-mannoside	SB	S	—
1 : 3-Butanediol	MB	S	—
Pentaerythritol	SB	S	—
Sucrose	FB	S	SS
Phenols			
Phenol	F	SS	—
Quinol	F	—	—
1 : 4-Dihydroxynaphthalene	F	S	—
Olefins			
Oct-1-ene	FB	CG	S
*cyclo*Hexene	FB	CG	—
1 : 2-Dimethyl*cyclo*hexene	S	S	—
1 : 2-Dimethyl*cyclo*pentene	FB	CG	—
2 : 4 : 4-Trimethylpentene	FB	C	—
Styrene	SS[S]B	—	—
Stilbene	[SS]	—	—
Triphenylethylene	O	—	—
Acrylonitrile	O	O	—
Methyl methacrylate	O	O	—
Ethers, etc.			
Diethyl ether	O	—	—
Dioxan	S	SS	—
Dibenzyl ether	M	—	—
tert.-Butyl hydroperoxide	FB	—	—
Di-*tert.*-butyl peroxide	O	—	—
Nitrogen compounds			
Aniline	FF	—	—
Ethylamine	S	—	—
Diethylamine	S	SS	—
Triethylamine	M	—	—
Ethylenediamine	S	SS	S
2-Hydroxyethylamine	S	SS	S
NN-Dimethylaniline	FF.B	—	—
Acetamide	O	—	—
Nitromethane	S[M]	—	—

Oxidation Test.—O = No reaction, SS = reaction very slow even on warming, S = reaction easy on warming, M = reaction slow in cold, F = reaction easy in cold, FF = reaction very rapid in cold, B = initial red or brown colour, possibly due to complex formation when substrate contains hydroxyl groups, or to the V^V hydroperoxide colour when traces of hydroperoxide may be present, H = oxidation occurred after standing for one month, D = red product formed during oxidation when ketone is in excess, [ ] = reaction carried out with 0·4N-V^V in 8N-H_2SO_4. Other reactions used 0·2N-V^V in 5N-H_2SO_4.

Polymerisation Test.—O = No polymerisation, SS = very slight cloudiness, S = definite cloudiness, C = thick polymer, G = test material polymerises itself. In no case did polymer appear before the initial red or brown colour, if any, had disappeared.

Mercuric Chloride Test.—SS = Very slight precipitate, S = slight precipitate, A = appreciable precipitate, C = considerable precipitate, O = no formation of mercurous chloride.

Oxidations involving vanadium(V) in solution are acid-dependent and due to a cationic form of vanadium, usually regarded as VO_2^+ aq.,[4] which forms bright yellow solutions in acidities over pH 1·5. Since both vanadic and vanadous salts are strong reducing agents the organic oxidations effected by vanadium(V) (pervanadyl) solutions proceed to the end-point of the blue vanadyl salt (V^{IV}), but every oxidation is not necessarily due to the one-electron transition $V^{V} \longrightarrow V^{IV}$. The alternative sequence $2e + V^{V} \longrightarrow V^{III}$ (slow); $V^{III} + V^{V} \longrightarrow 2V^{IV}$ (fast) has been suggested for certain inorganic oxidations.[3, 5]

In a preliminary survey (Table 1) we have used the two tests employed by Drummond and Waters[6] to characterise the oxidations effected by manganese(III), *viz.*, (*a*) induced polymerisation of vinyl cyanide and (*b*) induced reduction of mercuric chloride. Positive evidence of radical formation during the oxidations of aldehydes, ketones, α-hydroxy-acids, and some 1 : 2-glycols was obtained by both tests; with other compounds, *e.g.*, alcohols and olefins, catalysis of polymerisation occurs though the mercuric chloride test is not conclusive. In particular the oxidation of oxalic acid fails to induce the reduction of mercuric chloride, although the precipitate of mercurous chloride might be expected[6] to be especially copious in this instance. The often inconclusive nature of the mercuric chloride test does not disprove the presence of radicals, for it appears (see below) that vanadium(V) can react very rapidly with any radicals present, and so prevent their reduction of mercuric chloride. The polymerisation test certainly indicates that oxidations with vanadium(V) generally proceed by one-electron transitions, for vanadium-(IV) and -(III) could not initiate polymerisation under the conditions used, although the latter could do so in the presence of oxygen. However it would be premature to infer that all reactions involving reduction of vanadium(V) to vanadium(IV) by organic materials proceed by one-electron mechanisms. We propose to make a systematic survey of these reactions.

Our first example, the oxidation of pinacol, which we have already studied in detail, does however provide a clear example of a one-electron transfer process. We have found that (1) the reaction is quantitative according to the equation

$$(\cdot CMe_2\cdot OH)_2 + 2V^{V} = 2Me_2CO + 2V^{IV} + 2H^+$$

(2) it does catalyse the polymerisation of vinyl cyanide, and (3) it does produce radicals which can effect the reduction of mercuric chloride to mercurous chloride, but do not absorb free oxygen.

A kinetic study of this oxidation has been made by use of Morette and Gaudefroy's titrimetric procedure,[2] which, in daylight, proved to be more rapid and reliable at low concentrations than electrometric titration. Solutions of sodium or ammonium vanadate in aqueous sulphuric acid were used as the oxidiser, and, by the method of independent variation of both [pinacol] and [V^{V}], the reaction was shown to be of first order in vanadium up to 85% completion at least and also of first order in pinacol, as Tables 2 and 3 show.

Though vanadium(V) is amphoteric, it exists only as a cation in solutions of acidity greater than 0·05M. In sulphuric acid between 0·3M and 0·75M the rate of oxidation is independent of the acidity (Table 4) within experimental error, and shows a linear positive salt effect (Table 5) indicating that the rate-determining reaction is taking place between a neutral molecule and an ion.

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[4] LaSalle and Cobble, *J. Phys. Chem.*, 1955, **59**, 119.

[5] Ramsey, Colichman, and Pack, *J. Amer. Chem. Soc.*, 1946, **68**, 1695; Boyer and Ramsey, *ibid*, 1953, **75**, 3802; Kirson and Bobtelsky, *Bull. Soc. chim. France*, 1947, 560; Bobtelsky and Czosnek,. *Z. anorg. Chem.*, 1932, **205**, 401; **206**, 113; Krauze and Vorob'eva, *Sci. Rep. Moscow State University*, 1936, **6**, 5; Higginson, Sutton, and Wright, *J.*, 1953, 1380; 1402; Trujillo and Rios, *Anales real. Soc. españ. Fís. Quím.*, 1954, **49**, *B*, 473.

[6] Drummond and Waters, *J.*, 1953, 2836, 3119.

TABLE 2.

Dependence of rate on [V^V] *at* 25·0°.

[Pinacol] = 0·0968M.

[H_2SO_4] (M)	[V^V]initial (N)	10^4k (sec.$^{-1}$)
0·375	0·0099	2·31
0·425	0·0197	2·26
0·5	0·0495	2·36
0·75	0·0987	2·41

Mean value of $k = (2{\cdot}34 \pm 0{\cdot}05) \times 10^{-4}$ sec.$^{-1}$.

Individual experiments showed no significant departure from first-order kinetics up to 85% completion.

TABLE 3.

Dependence of rate on [*Pinacol*] *at* 25·0°

[Pinacol] (M)	10^4k	10^3k/[Pinacol]
0·0268	0·649	2·42
0·0535	1·18	2·21
0·0968	2·26	2·33
0·1775	4·49	2·53
0·2785	7·45	2·67
0·1135	2·75	2·42

Mean value of k/[Pinacol] = $(2{\cdot}43 \pm 0{\cdot}14) \times 10^{-3}$ mole^{-1} sec.$^{-1}$.

All experiments except the last were carried out in 0·35M-acid, with [V^V] = 0·02N and an atmosphere of air. The last was in 0·5M-acid with [V^V] = 0·05N and an atmosphere of nitrogen.

TABLE 4. *Dependence of rate on* [H^+] *at low acidities at* 25·0°.

[V^V] = 0·0494N, [Pinacol] = 0·0968M.

[H_2SO_4] (M)	0·3	0·375	0·5	0·75
10^4k	2·31	2·22	2·36	2·43

Mean value of $k = (2{\cdot}33 \pm 0{\cdot}11) \times 10^{-4}$ sec.$^{-1}$.

TABLE 5. *Dependence of rate on ionic strength at* 30·0°.

[Pinacol] = 0·032M, [V^V] = 0·0241N, [H_2SO_4] = 0·25M.

Ionic strength (M)	0·83	1·42	2·0
10^4k (sec.$^{-1}$)	1·4	1·63	1·91

The added salt was sodium chloride. Extrapolation gives $k = 1{\cdot}07 \times 10^{-4}$ sec.$^{-1}$ at zero ionic strength.

TABLE 6. *Dependence of rate on* [*Acrylonitrile*] *at* 25° *in nitrogen.*

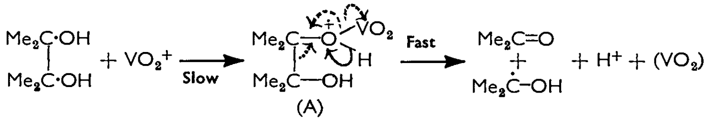
[Pinacol] = 0·1135M, [Acid] = 0·5M, [V^V] = 0·050N.

[Acrylonitrile] (M)	0·0	0·062	0·157	0·470	2·82
10^4k (sec.$^{-1}$)	2·75	2·96	2·82	2·92	3·55

The presence of polymer did not appear to affect the sampling technique or the accuracy of the titrations.

The foregoing information accords with the following mechanism, where (A) may be an irreversibly formed compound or transition complex, and (VO_2) is the basic oxide of the eventual vanadyl salt:

(1)



$$(2)\quad Me_2\dot{C}{\cdot}OH + VO_2^+ \xrightarrow{\text{Fast}} Me_2C{=}O + H^+ + (VO_2)$$

Now the oxidation of pinacol by manganic pyrophosphate [6] was retarded by the addition of vinyl cyanide, but, as Table 6 shows, the addition of vinyl cyanide has very little effect on the rate of oxidation of pinacol by vanadium(V), although a polymer containing hydroxyl groups is formed. Consequently the oxidation of the polymer radical (3) must be

$$(3)\quad Me_2C(OH){\cdot}[CH_2{\cdot}CH(CN)]_n{\cdot}CH_2{\cdot}CH(CN){\cdot} + VO_2^+ \longrightarrow \text{Polymer} + (VO_2)$$

so much faster than (1) that it does not affect the overall rate. The fact that polymer is formed indicates that reaction (4) must be faster than either (2) or (3).

$$(4)\quad Me_2\dot{C}(OH) + CH_2{:}CH{\cdot}CN \longrightarrow Me_2C(OH)CH_2{\cdot}CH(CN){\cdot}$$

In solutions of high sulphuric acid concentration however the oxidation is not so simple as eqns. (1) and (2) indicate, for the rate of reactions markedly increases at high acidities, as Table 7 and Fig. 1 show. H_0 was obtained from the figures of Paul and Long,[7] and $\alpha_{\pm}$ from the figures of Stokes.[8] k_0 was found to be $1{\cdot}31 \times 10^{-4}$ sec.$^{-1}$. Sulphuric acid can be assumed to be a strong, monobasic acid throughout this range.

TABLE 7. *Dependence of rate on acid concentration over an extended range of acidity at* 30°.

[Pinacol] = 0·032M, [$\mathrm{V^V}$] = 0·0241N.

[H_3O^+] (M)	0·05	0·25	1·2	2·15	3·05	4·0	4·95	5·85
H_0	1·0	0·44	−0·38	−0·93	−1·40	−1·85	−2·26	−2·68
$a \pm$	0·015	0·0495	0·154	0·278	0·436	0·68	1·02	1·46
10^4k (sec.$^{-1}$)	1·33	1·40	1·90	3·10	6·08	12·0	19·6	35·0

To elucidate this effect of strong acid the oxidation rate has been plotted against various acidity functions. Also the total rate constant k has been divided into two portions, k_0, a hydrogen-independent value obtained by extrapolating the measured rate to [H_3O^+] = 0, and k_1, an acid-dependent portion, such that $k = k_0 + k_1$; these have also been plotted against acidity functions (Figs. 1—4).

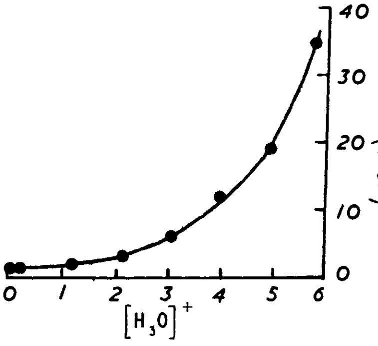


FIG. 1. *Dependence of the rate of the reaction of vanadium*(V) *with pinacol on acidity.*

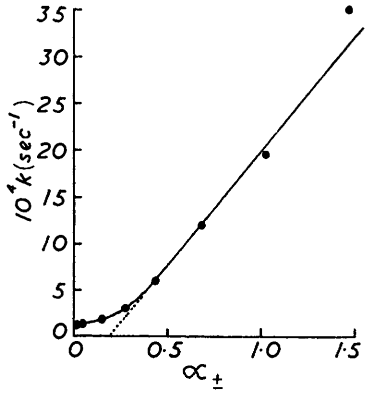


FIG. 2. *Dependence of the rate of the reaction of vanadium*(V) *with pinacol on the total activity of the acid,* $a_{\pm}$.

Potentiometric determinations of hydrogen-ion activity, a_{H^+}, in solutions identical with the reaction mixtures except for the omission of the organic substrate, a glass electrode and a calomel electrode being used, gave a curve very similar to that obtained when the mean activity of the acid ($\alpha_{\pm}$) is used (Fig. 2). The significance of such a_{H^+} measurements is, however, not great in solutions of the acidities used, and $\alpha_{\pm}$, though exact, is a mean function of both H_3O^+ and HSO_4^- ions. However the curve appears to be approximately linear in regions where the acid dependent reaction is most important.

Fig. 3 illustrates that the dependence of k_1 on total acid concentration [H_3O^+] is approximately of first order at the lower acidities, but the line has a positive curvature, and at high acidities is of second or higher order. Fig. 4 shows that if the Hammett function, H_0, is the relevant acidity function to correlate with log k_1 then a good first-order plot is obtained over a wide acidity range, but at really high acid concentrations the rate increases more slowly than direct proportionality requires.

To a first approximation the acid-dependence of the reaction can be explained by postulating the existence of an equilibrium (5), as suggested by Ramsey, Colichman, and Pack,[5]

$$(5)\quad \mathrm{VO_2^+} + \mathrm{H^+} \overset{K}{\rightleftharpoons} \mathrm{VO_2H^{2+}}$$

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[7] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.
[8] Stokes, *Trans. Faraday Soc.*, 1948, **44**, 295.

followed by (6):

$$(6)\quad \mathrm{VO_2H^{2+}} + \text{Pinacol} \xrightarrow{\text{Slow}} \text{Complex} \xrightarrow{\text{Fast}} \text{Products} + (\mathrm{VO_2})$$

the attack of the doubly charged cation which is a more powerful oxidiser than VO_2^+. When this is taken into account the rate equation for the acid-dependent reaction becomes

$$\frac{-d[V^V]}{dt} = \frac{k'K[V^V][H^+][\text{Pinacol}]}{1 + K[H^+]}$$

where $k'K = k_1$.

If $K \approx 1/[H^+]$ then a falling off from first-order dependence will result. This law can explain dependence on either $[H_3O^+]$ or the Hammett function h_0, for dependence on h_0 could be consistent with eqn. (5), and dependence on $[H_3O^+]$ would not be inconsistent with eqn. (5*A*):

FIG. 3. *Graphical determination of the order of the reaction of vanadium*(V) *with pinacol with respect to acid concentration. Curve A refers to total rate* (*k*), *curve B to acid-dependent rate* (k_1).

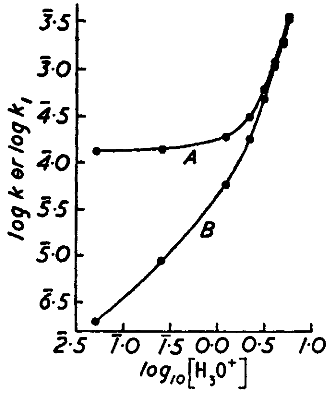
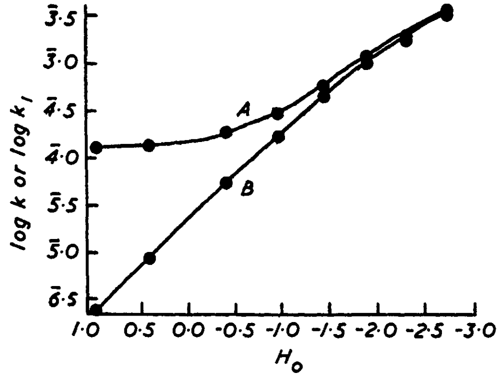


FIG. 4. *Graphical determination of the order of the reaction of vanadium*(V) *with pinacol with respect to the Hammett acidity function. Curve A refers to total rate* (*k*), *curve B to acid-dependent rate* (k_1).



$$(5A)\quad \mathrm{VO_2^+} + \mathrm{H_3O^+} \overset{K}{\rightleftharpoons} \mathrm{V(OH)_3^{2+}}$$

followed by attack on pinacol by $V(OH)_3^{2+}$.

In theory, the Hammett function h_0 is not the correct acidity function for use in connection with equilibrium (5), and it should be replaced by h_+, which is appropriate for addition of a proton to a cation. However values of H_+ are not available in strong sulphuric acid, and Bonner and Lockhart have shown [9] that in certain ranges H_0 and H_+ change in a parallel manner.

An alternative explanation of the acidity dependence at high acidity may however be adduced from the observation that as the strength of the acid is increased the colour of the vanadium(V) solution changes gradually from yellow to deep red. If this is due to a sulphate complex [10] then the curvature of either Fig. 3 or 4 could be accounted for, by suggesting (*a*) that the primary dependence is on $[H_3O^+]$ and that sulphate complex is a more powerful oxidising agent than the VO_2H^{2+} or $V(OH)_3^{2+}$ which it replaces, or (*b*) that the primary dependence is on h_0 and that the sulphate complex is a less powerful oxidiser. Salt effects may also affect the form of the dependence on acidity, for no attempt was made to keep the ionic strength constant.

Thus the observed kinetics accord with the equation

$$-d[V^V]/dt = k_0[V^V][\text{Pinacol}]\,\{1 + f([H^+])\}$$

where the precise reason for the form of $f([H^+])$ has not yet been established.

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[9] Bonner and Lockhart, *J.*, 1957, 364.

[10] Ducret, *Ann. Chim.* (*France*), 1951, **6**, 705.

EXPERIMENTAL

Qualitative Tests (*Table* 1).—Oxidation tests were carried out by adding an excess of the substance to a solution of vanadium(v) in sulphuric acid. Reduction of the vanadium to the blue of vanadium(IV) *via* green was observed visually.

Polymerisation Tests.—Acrylonitrile and the substrate were placed in the lower part of a Thunberg tube while vanadium(v) solution was placed in the top part. The tubes were evacuated, filled with pure dry nitrogen twice, and then evacuated again. If after 30 min. no polymer had formed the liquids were mixed, and, if necessary, warmed to 70° to accelerate oxidation. If polymer tended to form as a result of distillation within the tube, the latter was left filled with nitrogen. Every experiment was accompanied by a blank control.

Mercuric Chloride Test.—The substrate, saturated mercuric chloride solution, and vanadium(v) solution were mixed in a test-tube and examined after 18 hr. Only small quantities of a white precipitate of mercurous chloride were ever observed and the test was often obscured by cloudiness resulting from the oxidation. In a few cases the nature of the precipitate was confirmed by separating it and showing that it was blackened by ammonia.

Except for the olefins, all the substances listed are wholly or partially miscible with water, and so these oxidations are not controlled by solubility limitations. With the olefins, however, the rate is probably solubility-controlled. The oxidation of amines is noticeably acid-dependent, being stopped when the acid is too concentrated. Since acid concentrations were not carefully controlled, the relative rates of oxidation of the various amines has not definitely been established.

The possibility that vanadium-(III) or -(IV) might be able to initiate polymerisation was investigated by mixing a suitably reduced sample of the stock solution of vanadium with acrylonitrile. Neither valency state was capable of causing polymerisation in the absence of air, but if air was admitted to solutions containing V^{III} or mixtures of V^{III} and V^{IV} then a surface film of polymer formed. Uptake of oxygen by V^{III} solutions in the absence of monomer was confirmed by the Warburg technique. Dainton and James's [11] report on similar experiments is not entirely clear, but if in fact these investigators have found that solutions of V^{III} did not form a reduction–activation system with oxygen, then the discrepancy may perhaps be due to the greater acidity of the solutions used in the present work.

Materials.—*Vanadium*(v) *solutions.* For the qualitative work commercial sodium orthovanadate was dissolved or suspended in water and the calculated quantity of concentrated acid added. For the kinetic work B.D.H. Laboratory Reagent grade sodium metavanadate was used. "AnalaR" ferrous ammonium sulphate was used to prepare a standard solution against which the vanadium(v) solution was titrated. Acrylonitrile, freed from inhibitor by washing with alkali and water, was dried, and distilled under nitrogen. Pinacol was distilled, then recrystallised four times from distilled water. It was used as the dry hexahydrate, m. p. 46·5°.

Kinetic Measurements.—The reactions were carried out in a thermostat regulated to within ±0·05°. After measured time intervals, from 8 to 10 aliquot portions of reaction mixtures, which usually contained a large excess of one component, were each added in succession to a known excess of ferrous solution, and the excess of Fe^{2+} was titrated with V^V solution, barium diphenylaminesulphonate in the presence of phosphoric acid being used as indicator. The apparent rate constants were then evaluated from log $[V^V]$–time plots. When acrylonitrile was present the solutions were blown out with pure dry nitrogen before mixing, and nitrogen was passed through them during the reaction. Comparison of an experiment conducted under nitrogen with ones open to the air (see Table 3) indicated that oxygen was not interfering, and the absence of any oxygen uptake was confirmed by the Warburg technique.[12] No catalytic effect was detected when 0·0099M-ferric alum was present.

Investigation of Stoicheiometry.—A weighed sample of pinacol was oxidised overnight by a known excess of vanadium(v) solution and the remaining oxidant was then estimated. 1 mole of pinacol required 2·04 ± 0·03 equivalents of vanadium(v). After reduction of the excess of vanadium(v), 2 : 4-dinitrophenylhydrazine was added to the solution and acetone 2 : 4-dinitrophenylhydrazone, m. p. 128° (and mixed m. p. with an authentic specimen), was collected in 102% yield.

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[11] Dainton and James, *Trans. Faraday Soc.*, 1958, **54**, 649.

[12] Milton and Waters, "Methods of Qualitative Microanalysis," Arnold, London, 1949, pp. 562—573.