Oxidation of Some Organic Compounds with Standard Solutions of Quinquevalent Vanadium

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▶Exploratory oxidations of several organic compounds have employed acidic solutions of vanadium(V). α-Hydroxy acids appear to undergo a stoichiometric reaction with this reagent, the products being carbon dioxide and the corresponding carboxylic acid possessing one carbon atom less than the starting substance. Ethylene glycol, glycerol, and 1,3-propanediol are oxidized to formic acid; no simple stoichiometry is observed in the vanadium(V) oxidation of malonic acid and 1,2-propanediol.

In acid solution, vanadium(V) is a moderately strong oxidizing agent. While the possibility exists that reduction to any of several lower oxidation states may occur, conditions are readily achieved wherein vanadium(IV) is the sole product of this process:

$$VO_2^+ + e + 2H^+ \rightarrow VO^{++} + H_2O$$

Only in the past two decades have investigations been undertaken to develop volumetric analyses employing standard solutions of vanadium(V). Methods for the analysis of a variety of inorganic substances have been reported (*7–9*); much less is known regarding the quantitative behavior of vanadate solutions with respect to organic compounds. It has been reported that solutions of vanadium(V) quantitatively oxidize oxalic acid (*3*), tartaric acid (*5*), pyruvic acid (*3*), naphthalene and its sulfonic acid derivatives (*2*), hydroquinone (*4*), indigo and indigo carmine (*6*). Formic acid is slowly oxidized by acidic solutions of the reagent at elevated temperatures, while most of the higher saturated fatty acids are unaffected. Methanol, formaldehyde, and acetone are reported to undergo ready oxidation under similar conditions (*3*).

This investigation was undertaken to ascertain the action of acidic vanadium(V) solutions upon various organic compounds, particular reference being given to polyfunctional carboxylic acids and polyhydric alcohols. Formic and acetic acids, thought to be oxidation products in several instances, were tested.

Data were also obtained with regard to the stability of vanadium(V) solutions.

REAGENTS AND SOLUTIONS

Vanadium(V) Solutions. Approximately 0.3*N*. About 33 grams of C.P. ammonium metavanadate were dissolved in 900 ml. of distilled water and 100 ml. of concentrated sulfuric acid. The usual slight turbidity of these solutions was removed by filtration through sintered glass prior to standardization and use.

Ferrous Ammonium Sulfate. Mohr's salt solutions, approximately 0.12*N* in iron(II), were prepared by dissolving about 48 grams of ferrous ammonium sulfate hexahydrate in 1 liter of 10% sulfuric acid. The volume ratios of these with respect to vanadium(V) solutions were obtained by direct titration; where they were employed in the standardization of vanadate solutions, the concentrations were determined by titration with primary standard potassium dichromate in the presence of diphenylamine sulfonic acid as indicator.

***N*-Phenylanthranilic Acid.** A 0.066*F* solution of *N*-phenylanthranilic acid was a satisfactory indicator for the reaction between vanadium(V) and iron(II); this was prepared by dissolving 0.213 gram of the solid in 30 ml. of 5% sodium carbonate, followed by dilution to 150 ml. with distilled water. Three to five drops of the indicator solution were used for each titration.

Organic Compounds. In general, the several organic compounds tested were in the form of dilute aqueous solutions. Commercial formic, acetic lactic, and glycolic acids were used without further purification, the concentration of the dilute solutions being established by titration with carbonate-free sodium hydroxide. The source of oxalic acid was primary standard grade sodium oxalate. Samples of mandelic, maleic, fumaric, and malonic acids were recrystallized prior to preparation of dilute solutions. Commercial ethylene glycol and glycerol were employed without further purification, the concentration of the dilute solutions being obtained by dichromate or periodate oxidation. Solutions of 1,2- and 1,3-propanediol were prepared by dilution of weighed quantities of the freshly vacuum-distilled glycols.

PROCEDURE

Standardization of Vanadium(V) Solutions. A 10-ml. aliquot of vanadate solution is diluted with 100 ml. of distilled water and cautiously acidified with 25 ml. of concentrated sulfuric acid. The resulting solution is cooled to room temperature, and titrated with standard Mohr's salt solution to the appearance of a distinct blue. Three to five drops of *N*-phenylanthranilic acid are introduced, and the titration is continued until the purple of the oxidized form of the indicator changes to a bright green.

Vanadium(V) solutions may also be standardized against sodium oxalate (*11*).

Indicator Properties of *N*-Phenylanthranilic Acid Solutions. The rate at which the color change of the indicator occurs is prohibitively slow in media which are less than 1.5*F* in sulfuric acid; the foregoing procedure produces a 3*F* sulfuric acid solution and the color change is rapid. It is nevertheless advisable to introduce the reducing agent slowly at the end of the titration, to avoid overrunning of the end point. At room temperature the color change is reversible and it is equally feasible to employ the vanadate solution as the titrant, the indicator correction being negligible. Irreversible oxidation of *N*-phenylanthranilic acid by vanadium(V) occurs at elevated temperatures. The intense blue of vanadium(IV) in a concentrated solution interferes with observation of the color change of the indicator but dilution of the sample with water prior to titration eliminates this.

Oxidation of Organic Compounds. This procedure involved the treatment of 10-ml. aliquots of a dilute aqueous solution of the organic compound with a known excess of vanadium(V) contained in an equal volume. Sulfuric acid was added in the desired amount; the samples were then heated in a boiling water bath. At suitable time intervals the samples were removed, and the reaction was stopped by dilution of the mixture with 100 ml. of distilled water and cooling. Additional sulfuric acid was added as necessary to give a solution

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3.6*F*, following which the excess vanadate was titrated with standard Mohr's salt solution.

Erlenmeyer flasks of 250-ml. capacity were generally used for the oxidations. Because no provision for reflux was made, the volume of the reaction mixtures decreased considerably over prolonged heating periods. When reference is made to the acidity of a reaction mixture, this relates to the acid concentration existing at the onset of heating.

RESULTS AND DISCUSSION

The oxidation of several carboxylic, dicarboxylic, and α-hydroxy acids as well as a number of simple polyhydric alcohols was studied. In each case the number of equivalents of vanadium(V) consumed per formula weight of organic compound was calculated as a function of such variables as temperature, sulfuric acid concentration, and time of reaction. The results of these experiments gave some indication of the reaction rate as well as the stoichiometry. In most cases, with a sufficient heating period the consumption of vanadium(V) became constant and independent of time. Where this limiting value approached that of an integer, a single reaction was suspected; in these instances, attempts were made to isolate the products and confirm the stoichiometry of the reaction.

Formic Acid, Acetic Acid. Table I gives the results of experiments in which formic acid was heated in the presence of an excess of vanadium(V) and at several sulfuric acid concentrations. This substance is not indefinitely stable to attack by the oxidizing agent, particularly at elevated temperatures and in highly acidic media. Because formic acid is a product in several of the oxidations studied, this slow reaction with vanadium(V) assumes considerable importance. To obtain a quantitative reaction in instances where this substance is produced, experimental conditions must be imposed so that this effect is negligible.

Acetic acid was unaffected when heated for 1 hour with an excess of vanadate in a medium initially 9.9*F* as to sulfuric acid.

α-Hydroxy Acids. On the basis of three hydroxy acids investigated, the vanadium(V) oxidation of this class of compounds appears to involve the formation of equimolar quantities of carbon dioxide and the carboxylic acid possessing one carbon atom less than that of the parent substance, a process which calls for the consumption of four equivalents of oxidant:

$$\mathrm{RCHOHCOOH + 4VO_2^+ + 4H^+ \rightarrow}$$
$$\mathrm{RCOOH + CO_2 + 4VO^{++} + 3H_2O}$$

Table I. Vanadate Oxidation of Formic Acid at 100° C.

(0.795 mmole of formic acid present in each sample)

Quantity of Reagent Initially Present		Heating Time, Min.	Ml. of 0.300*N* Vanadate Solution Used
Vanadium-(V), meq.	Sulfuric acid, *F*		
3.450	8.7	0[a]	0.02
	9.7	0	0.06
	10.1	0	0.13
	10.4	0	0.15
	11.4	0	0.41
3.460	5.2	10	0.04
	9.2	10	0.11
2.847	0.82	51	0.06
	4.5	56	0.09

[a] Samples of this series allowed to stand for 5 minutes prior to dilution; only heat supplied was that accompanying addition of sulfuric acid to vanadium(V)–formic acid solutions.

Table II. Vanadate Oxidation of Mandelic Acid

(0.858 mmole of mandelic acid, 5.147 meq. VO_2^+ present)

Concn. Sulfuric Acid, *F*	Equivalents of Vanadate Consumed per Gram Formula Wt. of Mandelic Acid over Time Interval, Room Temp.	
	30 min.	60 min.
0.90	3.12	3.09
2.5	3.61	3.58
3.8	3.78	3.77
4.8	3.84	3.85
5.8	3.86	3.86
6.6	3.87	3.90
7.3	3.79	3.86

Table III. Vanadate Oxidation of Glycolic Acid in 9.9F Sulfuric Acid

(0.288 mmole of glycolic acid, 2.718 meq. VO_2^+ present)

Heating Time at 100° C., Min.	Equivalents of Vanadate Consumed per Gram Formula Wt. of Glycolic Acid
0	4.01
5	4.01
15	4.04
20	4.07
40	4.08
60	4.11
120	4.21

Table IV. Vanadate Oxidation of Lactic Acid

(Initial sulfuric acid concn. 6.6*F*; 3.192 meq. VO_2^+ present)

Lactic Acid, Mg.		Relative Error	
Taken	Found	%	Av.
9.05	9.21	1.8	
8.97	9.12	1.7	1.8
17.3	17.5	1.2	
17.8	17.9	0.6	0.9
26.0	26.2	0.8	
25.0	25.2	0.8	0.8
35.0	35.2	0.6	
35.7	35.9	0.6	0.6
43.4	43.6	0.5	
43.0	43.2	0.5	0.5
51.2	51.3	0.2	
52.4	52.5	0.2	0.2
61.2	61.1	0.2	
60.8	60.7	0.2	0.2
69.8	69.2	0.9	
69.9	69.3	0.9	0.9

Table II summarizes the findings relative to the oxidation of mandelic acid; benzoic acid was isolated and identified as a product of the reaction. Oxidation occurs readily at room temperature, the extent of the reaction being independent of the sulfuric acid concentration above 4*F*. Consumption of oxidant was 2.5 to 5% short of theoretical; this may be due to the presence of impurities in the sample of mandelic acid rather than to its incomplete oxidation.

In a medium initially 9.9*F* with respect to sulfuric acid, glycolic acid is very rapidly oxidized by an excess of vanadium(V), as indicated in Table III. The data are consistent with the proposed general equation for the oxidation of this class of substances, equimolar quantities of carbon dioxide and formic acid being produced; this substance could readily be analyzed by use of this reaction.

Lactic acid could be quantitatively oxidized by heating samples for 6 minutes or more in a boiling water bath when the initial sulfuric acid concentration was held within the range between 5 and 8*F*. Four equivalents of vanadate are consumed per formula weight of lactic acid, corresponding to the formation of equimolar amounts of carbon dioxide and acetic acid. On the basis of these studies, a method was evolved for the analysis of this substance; the method gave results with a relative error of less than 1% over an approximately fourfold range of concentration of lactic acid. Representative analytical data are given in Table IV.

Recommended Procedure for Vanadium(V) Oxidation of Lactic Acid. An excess of 0.3*N* vanadate solution, in the form of a 10-ml. aliquot, is cautiously acidified with 10 ml. of concentrated sulfuric acid and the mixture cooled to room temperature. To this is added 10 ml. of a solution containing between 17 and 70 mg. of lactic acid. After thorough mixing, the resulting solution is heated in a boiling water bath for approximately 10 minutes. The sample is then diluted with 100 ml. of distilled water and cooled to room temperature. An additional 15 ml. of sulfuric acid is introduced prior to titration of the excess vanadium(V) in the sample with a standard Mohr's salt solution. *N*-phenylanthranilic acid is employed as indicator, the color change from violet to green being taken as the end point.

Maleic Acid, Fumaric Acid. To observe the differences in behavior between maleic and fumaric acids, care was taken to prepare and treat samples of the two identically. Table V shows the results obtained from the oxidation of these geometric isomers with vanadium(V) under a variety of conditions. Oxidation of either to carbon dioxide and water would require 12 equivalents of oxidant per gram formula weight of the acid; this, in fact, appears to be the course of these reactions when the reaction mixtures are vigorously heated. Under milder conditions, the cis-isomer is slowly oxidized, an apparent limiting value for oxidant consumption of 8 equivalents per formula weight being approached; probable oxidation products of this reaction are two formula weights each of carbon dioxide and formic acid for every gram formula weight of maleic acid reactive. In the same period of time and under identical conditions, the oxidation of fumaric acid is approaching a value of 2 equivalents of vanadium(V) used per formula weight of the acid. It is likely that the fact that this value approximates a whole number is fortuitous; a 2-electron oxidation of fumaric acid would almost certainly involve the opening of the double bond, with production of the corresponding dihydroxy acid, tartaric acid, which undergoes rapid oxidation with vanadium(V) under these conditions. It thus seems more likely that this difference in behavior is one of reaction rate, rather than any difference in stoichiometry.

Oxalic Acid, Malonic Acid. In 9.9*F* sulfuric acid, the oxidation of oxalic acid to carbon dioxide is rapid and quantitative; details of a method which permits use of sodium oxalate as a primary standard for vanadium(V) solutions have been published (*11*).

Under the same reaction conditions, the next member of this series shows no simple stoichiometry; oxidation of malonic acid to carbon dioxide and water would require 8 equivalents of oxidant per gram formula weight of the acid, while production of two formula weights of carbon dioxide and one of formic acid would involve the use of but 6 equivalents. The experimentally obtained value for this ratio approaches a limit which lies between these figures, as indicated in Table VI. It is likely that both processes occur simultaneously; a 6 to 1 stoichiometry might result from the use of milder oxidizing conditions.

Table V. Vanadate Oxidation of Maleic and Fumaric Acids

(0.289 mmole of maleic or fumaric acid, 5.45 meq. VO_2^+ present)

Concn. of Sulfuric Acid, *F*	Equivalents Vanadate Used / GFW of Acid		Mode of Heating
	Maleic	Fumaric	
3.7	9.85	9.86	Boiled 30 min.
3.7	8.66	6.16	Heated to evolution of SO_3
5.8	10.34	11.04	
3.7	0.76	0.73	60 min. at 100° C.
5.8	3.78	0.63	30 min.
5.8	5.54	0.96	60 min.
5.8	6.30	1.33	90 min.
5.8	7.16	1.28	120 min.
5.8	7.86	1.92	210 min.

Table VI. Vanadate Oxidation of Oxalic and Malonic Acids in 9.9*F* Sulfuric Acid

(0.863 to 1.020 mmole of oxalic acid, 3.018 meq. VO_2^+; 0.212 mmole of malonic acid, 2.718 meq. VO_2^+ present)

Heating Time at 100° C., Min.	Equivalents of Vanadate Consumed per Gram Formula Wt. of Substance	
	Oxalic acid	Malonic acid
5	2.01	6.02
10	. . .	6.64
15	2.00	6.79
30	2.00	7.29
60	2.01	7.35
90	. . .	7.35
120	. . .	7.40

Table VII. Vanadate Oxidation of Several Polyhydric Alcohols in 9.9*F* Sulfuric Acid

Heating Time at 100° C., Min.	Equivalents of Vanadate Consumed per Gram Formula Wt. of Substance			
	Ethylene glycol[a]	1,3-Propanediol[b]	1,2-Propanediol[c]	Glycerol[d]
0	0.72	. . .	0.75	4.90
5	4.77	. . .	5.95	8.38
10	5.21	7.73	6.47	8.45
15	5.37	8.09	6.81	8.46
30	5.75	8.79	7.06	8.45
45	5.87	9.24	7.15	. . .
60	5.98	10.08	7.08	8.53
75	6.01	. . .	7.18	8.58
90	6.01	10.12	. . .	8.72
120	6.13	. . .	. . .	8.78

[a] 0.323 mmole of ethylene glycol, 2.887 meq. VO_2^+ present.
[b] 0.146 mmole of 1,3-propanediol, 2.928 meq. VO_2^+ present.
[c] 0.200 mmole of 1,2-propanediol, 2.902 meq. VO_2^+ present.
[d] 0.177 mmole of glycerol, 2.718 meq. VO_2^+ present.

Table VIII. Stability of Vanadate Solutions

Time Since Preparation, Days	Concentration of Vanadate		Change in Concentration, %
	Equivalents per liter	Av. dev.	
77	0.2809	0.0002	. . .
159	0.2811	0.0003	0.1
366	0.2805	0.0003	0.1
377	0.2807	0.0001	0.1
1	0.1108	0.0001	. . .
342	0.1111	0.0001	0.3
347	0.1110	0.0001	0.2
6	0.3077	0.0002	. . .
8	0.3073	0.0002	0.1
50	0.3078	0.0003	0.0
55	0.3072	0.0002	0.2
8	0.3177	0.0001	. . .
12	0.3180	0.0002	0.1
15	0.3173	0.0001	0.1
38	0.3180	0.0002	0.1

Polyhydric Alcohols. Table VII shows the results obtained from a series of oxidations of ethylene glycol with vanadium(V) in 9.9*F* sulfuric acid. The consumption of vanadate attains an essentially constant value of 6 equivalents per formula weight of glycol for heating periods in excess of 1 hour at 100° C. An equation may be written which expresses these findings:

$$HOCH_2CH_2OH + 6VO_2^+ + 6H^+ \rightarrow 2HCOOH + 6VO^{++} + 4H_2O$$

Formic acid was the product of this oxidation. Approximately 90% of the theoretical quantity of this substance was recovered by prolonged steam distillation of the reaction mixtures; the identity of the acid was established by potentiometric titration and by preparation of the *S*-1-naphthylmethylthiuronium derivative from the sodium salt (*1*).

Also shown in Table VII are data

relating to the oxidation of 1,3-propanediol and 1,2-propanediol with vanadium(V) in a medium initially 9.9*F* in sulfuric acid.

Under these conditions each formula weight of 1,3-propanediol requires 10 equivalents of vanadate. An equation which accounts for this finding involves the production of formic acid:

$$HOCH_2CH_2CH_2OH + 10\ VO_2^+ + 10\ H^+ \rightarrow 3\ HCOOH + 10\ VO^{++} + 6\ H_2O$$

The intermediate formation of malonic acid does not appear to be involved in this process; on the basis of experiments with the latter substance, a vanadate consumption in excess of 15 equivalents per formula weight of 1,3-propanediol would have been expected, had its production occurred in the course of this reaction.

The effect of the relative position of the hydroxyl groups is demonstrated by comparing these data with those for the oxidation of 1,2-propanediol under identical conditions. Were this reaction to take the expected course, with the production of equimolar quantities of formic and acetic acids, 6 equivalents of oxidant would be required. The extent of oxidation found experimentally is considerably in excess of this figure; no simple stoichiometry can be proposed to explain these data.

As seen from Table VII, the oxidation of glycerol in a medium 9.9*F* in sulfuric acid involves the consumption of vanadium(V) significantly in excess of that required for oxidation to three formula weights of formic acid. Further study has shown that this difficulty can be eliminated by a suitable choice of reaction conditions, and that glycerol may be successfully analyzed through the use of this oxidizing agent (*10*).

Stability of Vanadium(V) Solutions. In connection with these studies, considerable information was accumulated as to the stability of acidic vanadate solutions on normal storage in clear, soft glass bottles for extended periods of time; representative data are given in Table VIII. The normality values represent the average of several titrations; reproducibility is indicated by the average deviation occurring between results in each standardization. Given also is the percentage change in concentration since the initial standardization.

These solutions retained essentially the same titer throughout test periods which ranged from 1 month to 1 year. No consistent trend of increase or decrease in normality can be noted. The differences observed between values in any set more likely reflect uncertainties in concentration of the solutions used for standardization rather than a tendency for the vanadium(V) solutions to change in normality.

These exploratory investigations indicate that the use of vanadium(V) solutions for the volumetric analysis of organic compounds is feasible in several instances. No specificity of action can be detected from the data presented; this drawback is common to many oxidizing agents in current use. Oxidative procedures with vanadium(V) solutions are simple, however, and close control of the variables of temperature and acid concentration does not appear to be critical. Finally, the ease of preparation of the reagent and its excellent stability warrant further consideration of its applicability in the analysis of organic compounds.

LITERATURE CITED

(1) Bonner, W. A., *J. Am. Chem. Soc.* **70**, 3508 (1948).

(2) Calcott, W. S., English, F. L., Downing, F. B., *Ind. Eng. Chem.* **16**, 27 (1924).

(3) Morette, André, Gaudefroy, Ghisdain, *Compt. rend.* **237**, 1523 (1953); *Bull. soc. chim. France* **21**, 956 (1954).

(4) Rao, G. G., Rao, V., Narasimha Sastri, M., *Current Sci. (India)* **18**, 381 (1949).

(5) Rao, G. G., Sankegowda, H., *Ibid.*, **21**, 188 (1952).

(6) *Ibid.*, p. 189.

(7) Singh, Balwant, Singh, Ranjit, *Anal. Chim. Acta* **10**, 408 (1954); **11**, 412 (1954).

(8) Singh, Balwant, Singh, Suyjit, *Ibid.*, **13**, 405 (1955).

(9) Tsubaki, Isamu, *Nippon Kagaku Zassi* **66**, 10 (1945); *Nippon Kagaku Zasshi* **71**, 454 (1950).

(10) West, D. M., Skoog, D. A., ANAL. CHEM. **31**, 586 (1959).

(11) West, D. M., Skoog, D. A., *Anal. Chim. Acta* **12**, 301 (1955).

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Analysis of Dilute Aqueous Glycerol Solutions with Quinquevalent Vanadium

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▶ A method for the analysis of glycerol is based on its oxidation to formic acid by acidic solutions of vanadium(V). The reaction is carried out in the presence of an excess of the oxidizing agent, such excess being determined by back-titration with a ferrous iron solution. Within the range of applicability, results accord well with those obtained by periodate, cerate, and dichromate oxidation.

GLYCEROL may be quantitatively analyzed in several ways, the method chosen depending in part upon the nature of the sample. When a small quantity of water is the principal impurity, as in refined glycerol, the assay is commonly carried out by a specific gravity measurement (*4*) or Karl Fischer titration (*5*). Crude glycerol samples and dilute aqueous solutions are more readily analyzed by oxidative methods employing dichromate (*1*), quadrivalent cerium (*7*), periodate (*3*), iodate (*8*), or permanganate (*6*). In addition, acetylation (*9*), the reaction of glycerol with hydriodic acid (*12*), and the formation of a sodium cupri–glycerol complex (*2*) have been used.

During an investigation of the oxidation of organic compounds with standard solutions of quinquevalent vanadium (*10*), conditions were found under which glycerol is stoichiometrically oxidized according to the equation:

$$HOCH_2CHOHCH_2OH + 8VO_2^+ + 8H^+ \rightarrow 3HCOOH + 8VO^{++} + 5H_2O$$

This reaction has been critically studied to evaluate its usefulness as an analytical method. It is carried out in the presence of an excess of the oxidizing agent, such excess being determined by back-titration with a ferrous ammonium sulfate solution of known titer in the presence of *N*-phenylanthranilic acid as indicator.

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