and degradation are simultaneous reactions, taking place in parallel. The elucidation of the exact mechanism, however, requires further study.

Although not yet experimentally tested, the authors believe that this degradation reaction should be a general one for aliphatic aldehydes. Further work on this point is also desirable.

Summary

Heptaldehyde was hydrogenated with a nickel catalyst at 250° under atmospheric pressure. A degradation reaction was observed. The main product was found to be n-hexane, some n-heptyl alcohol also being obtained. The carbon monoxide formed was partially reduced to methane.

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The Rate of Reduction of Vanadium Pentoxide in Concentrated Acid Solutions. Reduction of Vanadium Pentoxide by Arsenious Acid, Oxalic Acid, Formaldehyde and Ethyl Alcohol*

BY M. BOBTELSKY AND A. GLASNER

Pentavalent vanadium can be reduced to the tetravalent stage by many reducing agents almost all of which react only in acid solutions. The literature on this subject is rather poor,[1,2,3] since it deals primarily with analytical questions. The aim of this article is to present a preliminary study of the reduction of pentavalent vanadium by four different reducing agents.

1. **Experimental.**—The solutions for the experiments were made up in small glass-stoppered flasks kept in a thermostat. In all experiments a $2/3$ M solution of Na-VO$_3$·4H$_2$O (Merck) was used. The total volume of the reacting solutions was always 20 cc., reduced to a minimum because we were working in highly concentrated solutions. Solutions containing sulfuric acid were prepared from concentrated acid (96%) by calculating the contraction of sulfuric acid solutions from tables in Landolt and Börnstein. A few experimental controls have shown that the difference between the calculated and real volumes never amounted to more than 1%. The reducing agent always was introduced in a large excess, at least five times above the amount necessary for a complete reduction of pentavalent to tetravalent vanadium. The thermostat was kept at a constant temperature of 30° (±0.1°), unless otherwise stated. The time of reaction was counted from the moment the last reagent was introduced into the flask. At known intervals 2 cc. of the solution was pipetted out with precise micropipets into 13 cc. of distilled water, thus diluting the solution and greatly reducing the velocity of the reaction, even stopping it altogether. The extinction of a 50-mm. column of the diluted solution was measured with a Hellige panphotometer, equipped with colored filters at the approximate wave lengths of 660 and 690 mμ.

(The two measurements served as a control for each other, giving good agreement; they gave a maximum difference of 2%.) The extinction thus measured was proportional to the concentration of blue tetravalent vanadium (as we ascertained in a large number of various acid solutions). The reacting solutions were originally yellow-orange to red color (depending predominantly on the acid concentration), turned green with time (even a small amount of vanadium pentoxide in a highly concentrated acid solution of tetravalent vanadium imparted a green color to the solution) and occasionally showed a very dark appearance. Two cc. of the dark green solution gave a blue color when diluted with 13 cc. of water. After the reduction was complete (from a day or two up to a week) the reacting solution had a blue-violet color.

2. **Reduction of Vanadium Pentoxide with Arsenious Acid.**—Various compounds of vanadium pentoxide and arsenic pentoxide have been known since Berzelius. Since then many have worked on these compounds, but very few have even as much as mentioned that vanadium pentoxide was reduced by arsenious oxide under certain conditions.[4,5,6]

For the preparation of solutions containing various amounts of arsenious oxide, a stock solution of 1 M arsenious oxide in 5.16 N sodium hydroxide was used. In order to study the influence of strong acids on the velocity of the reduction, two series of experiments with hydrochloric and sulfuric acids were made. The reaction solutions in each experiment contained 3 cc. of $2/3$ M NaVO$_3$ + 2.5 (or 5) cc. of As$_2$O$_3$ + x cc. of acid; the total volume was 20 cc. In all experiments with arsenious acid, on calculating the final concentration of the acid an appropriate correction for the sodium hydroxide in the arsenious oxide solution was applied, but no correction for arsenious or vanadic acid was made. The vanadium was clearly reduced by arsenious acid at a measurable rate (in contradiction to R. Lang[6]). The results are given in Table I.

* Original manuscript received May 9, 1941.

(1) M. Bobtelsky and S. Czosnek, Z. anorg. allgem. Chem., **205**, 401–13; **206**, 113–24 (1932).

(2) M. Bobtelsky and L. Chajkin, ibid., **209**, 95–104 (1932).

(3) E. F. Krauze and O. I. Vorobieva, Sci. Rep. Moscow State Univ. No. **6**, 5–13 (1936).

(4) A. Ditte, Compt. rend., **101**, 1487 (1885).

(5) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, p. 199.

(6) R. Lang, Z. anorg. allgem. Chem., **152**, 205 (1926).

TABLE I

	2.5 cc. As₂O₃		5.0 cc. As₂O₃	
	Final N	$t_{1/2}$ in minutes	Final N	$t_{1/2}$ in minutes
H₂SO₄	0.85	114		
	1.60	102	1.60	48.0
	2.35	66.5	2.35	33.5
	3.10	44.0		
	3.85	29.0		
	4.60	20.0		
	5.35	12.5		
HCl	0.85	182		
	1.75	83.5	1.75	42.5
	2.35	41.5	2.35	20.0
	2.95	20.0		
	3.55	9.5		

Except at the very lowest acid concentrations, an arithmetic increase in acid concentration produced a geometric rise in velocity; for each increase of 0.75 N sulfuric acid the velocity was $^3/_2$ as much and for each increase of 0.6 N hydrochloric acid the rate was slightly more than twice as much. The influence of hydrochloric acid, in agreement with later results with other reductants, was greater than that of sulfuric acid.

The Order of Reaction.—The influence of arsenious acid concentration on the reaction rate can be seen in Table I. The time of half reaction found by measuring the V^{IV} concentration, was inversely proportional to the concentration of the arsenious oxide, from which it can be concluded that the reaction is *monomolecular*. The dependence of the reaction rate on the concentration of vanadium pentoxide is shown in Table II. All the solutions contained 2.5 cc. of arsenious oxide. Here $t_{1/2}$ was inversely proportional to the vanadium concentration. The reaction is therefore *bimolecular* toward V^V, and the reaction measured is $2V^V + As^{III} \rightarrow 2V^{IV} + As^V$.

TABLE II

H₂SO₄ final concn. (N)	NaVO₃ $^2/_3$ M in cc. (y)	$t_{1/2}$ in minutes	$t_{1/2} \times y$
1.6	3.0	103	309
1.6	4.0	75	300
3.85	2.0	46	92
3.85	4.0	21	84

Temperature Coefficient.—On comparing some experiments at 20° and 30° the temperature coefficient of 1.9 was obtained.

The influence of additional electrolytes on the reaction rate has been studied, but none of the cations, even those of changing valences as Mn^{++}, Cu^{++}, or Fe^{+++} (from concentrations of $N/5$ and less), exerted any catalytic influence; nor did nitric acid (which accelerated the reduction of vanadium with formaldehyde) show any special effect. On the other hand, phosphoric acid was
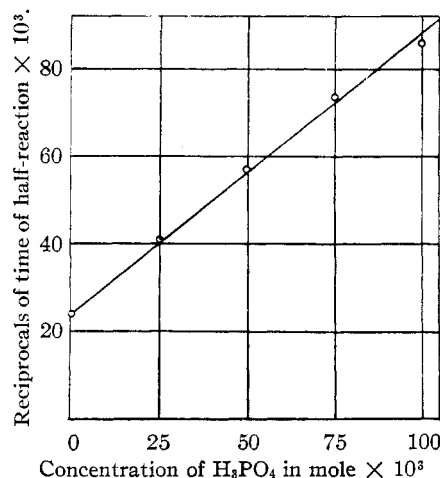

Fig. 1.—Influence of phosphoric acid on the rate of reduction of vanadium pentoxide by arsenious acid.

found to catalyze the reduction with arsenious oxide. The results of a series of experiments of the general composition: 3 cc. $^2/_3$ M NaVO₃ + 2.5 cc. As₂O₃ + 10 cc. 6 N HCl + x cc. M H₃PO₄ + $(4.5 - x)$cc. H₂O, are plotted in Fig. 1. The velocity of the reaction is *directly proportional* to the concentration of phosphoric acid. It is of interest to note that the action of phosphoric acid is more prominent in *low* concentrations of the strong acid (hydrochloric acid), as can be seen in Table III.

TABLE III

HCl final concn. (N)	Concn. of H₃PO₄, M	$t_{1/2}$ in minutes	Velocity ratio
0.85	0.0	182	
0.85	.1	23	7.9
2.35	.0	41.5	
2.35	.1	11.6	3.6

3. The Reduction of Vanadium Pentoxide with Oxalic Acid.—Vanadium pentoxide was reduced by oxalic acid even in dilute acid solutions. A. Rosenheim published a number of works on this reaction and proposed to use it for the estimation of vanadium.[7] *The influence of strong acids* was studied in a series of solutions of the following composition: 3 cc. $^2/_3$ M NaVO₃ + 5 cc. M H₂C₂O₄ + x cc. acid + $(12 - x)$ cc. H₂O. The results are plotted in Fig. 2. (When calculating the final acid concentration no correction for oxalic acid was made.) As is clearly seen, the rate of reduction decreased linearly with the increase in acid concentration up to a maximum of 3.4 N in hydrochloric acid and 7.8 N in sulfuric acid solutions. At concentrations above these the

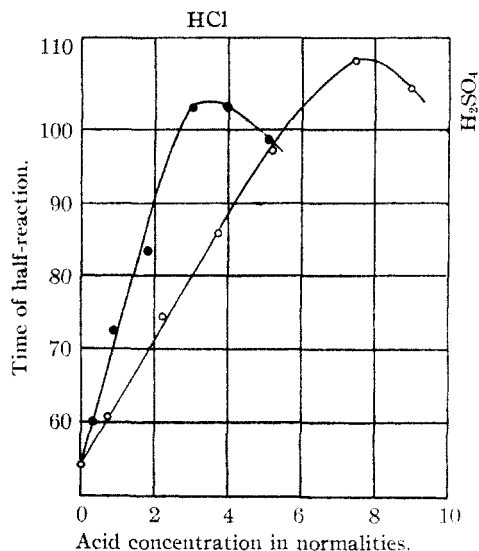(7) A. Rosenheim and Friedheim, *Z. anorg. allgem. Chem.*, **1**, 313–17 (1892).

Fig. 2.—Rate of reduction of vanadium pentoxide by oxalic acid in hydrochloric or sulfuric acid solutions.

acid effect was reversed. $t_{1/2}$ max. was almost equal for the two acids, but the inclination of the hydrochloric acid line was twice that of the sulfuric acid line. We observed this decrease of velocity with increase in acid concentration only in the case of oxalic acid. (Similar phenomena have been observed by other investigators in the oxidation of oxalic acid with chromic anhydride.[8]) It should be noted here that vanadium pentoxide is attacked by hydrochloric acid only in highly concentrated solutions. By blank experiments with hydrochloric acid, 6.85 N, which was the highest concentration used in this work (composition: 3 cc. $^2/_3$ M NaVO$_3$ + 12 cc. concd. HCl + 5 cc. H$_2$O), we established the fact that no traces of chlorine were liberated either at room temperature during an action for a week, or at 50° during two hours.

The Order of Reaction.—For the purpose of studying the order of reaction, a series of solutions of the following composition was prepared: 3 cc. $^2/_3$ M NaVO$_3$ + x cc. H$_2$SO$_4$ + y cc. H$_2$C$_2$O$_4$ + (17 − x − y) cc. H$_2$O. The results are given in Table IV. The cc. of oxalic acid marked in the table is equal to the number of times the reducing agent in the solution is in excess of the amount necessary for a complete reduction of penta- to tetra-valent vanadium. The influence of oxalic acid on $t_{1/2}$ is large and, as the table shows, the empirical formula $t_{1/2} \times y^2$ gives fairly good constants. On calculating the course of the individual reactions by the formula of the first

(8) N. Dahr, J. Chem. Soc., 707–762 (1917).

order: $k = 1/t \log a/(a − x)$, good constants were obtained only in solutions which contained the oxalic acid in very great excess. The constants also improved with the increase of strong acid concentration.

TABLE IV

cc. (y) of M H$_2$C$_2$O$_4$	H$_2$O $t_{1/2}$ min.	$t_{1/2}$ y^2	0.75 N H$_2$SO$_4$ $t_{1/2}$ min	$t_{1/2}$ y^2	3.75 N H$_2$SO$_4$ $t_{1/2}$ min.	$t_{1/2}$ y^2
5.0	54	1350	60.5	1512	84	2100
7.5	..	....	25.0	1406	42	2362
10.0	9.4	940	13.5	1350	24	2400

The Influence of Fe^{+++} and Mn^{++} Cations.— Preliminary experiments have proved that these two cations have a special influence on the reaction of pentavalent vanadium with oxalic acid. In order to investigate the Fe^{+++} ion effect, the following series of solutions was prepared: 3 cc. NaVO$_3$ + 5 cc. M H$_2$C$_2$O$_4$ + 5 cc. 15 N H$_2$SO$_4$ + x cc. Fe$_2$(SO$_4$)$_3$ + (7 − x) cc. H$_2$O. These experiments were made in flasks covered with black lacquer, as a necessary precaution to prevent the reduction of ferric ion by oxalic acid in the influence of light. Table V gives a résumé of the results. It seems that even in strongly acid solutions (3.75 N sulfuric acid) a complex is formed between ferric iron and oxalic acid which retards the reduction of vanadium. The time of half reaction is approximately proportional to the concentration of ferric sulfate, but if light fell on the reaction flasks the reduction was greatly accelerated. It is clear that in this case the iron was first reduced by oxalic acid by the action of light and this in turn reduced the vanadium. In order to investigate the Mn^{++} ion effect, a series of solutions of the following composition was prepared: 3 cc. $^2/_3$ M NaVO$_3$ + 5 cc. M H$_2$C$_2$O$_4$ + x cc. 15 N H$_2$SO$_4$ + y cc. 4 N MnSO$_4$ + (12 − x − y) cc. H$_2$O. The results are plotted in Fig. 3, from which the following conclusions can be drawn. The catalyst causes a linear rise in reaction velocity in the more concentrated acid solutions (3.75 and 7.5 N), but there is only a slow rise in the less concentrated

TABLE V

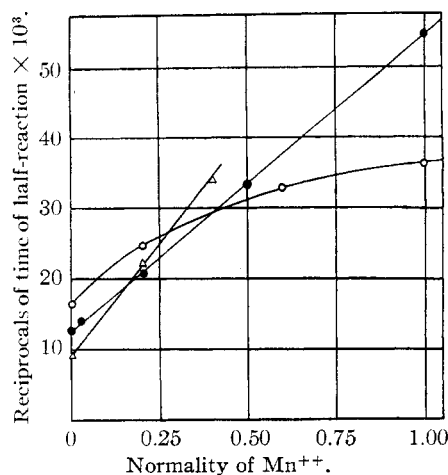| Fe$_2$(SO$_4$)$_3$, final normality	$t_{1/2}$ in minutes	Fe^{+++}/H$_2$C$_2$O$_4$
0.00	90	....
.05	108	1/15
.10	127	2/15
.15	149	3/15
.25	218	5/15
.50	440	10/15

Fig. 3.—Rate of reduction of vanadium pentoxide by oxalic acid in presence of Mn^{++} ions in sulfuric acid solutions: O, H$_2$SO$_4$, 0.75 N; ●, H$_2$SO$_4$, 3.75 N; Δ, H$_2$SO$_4$, 7.50 N.

acid solutions. The sensitivity of the catalyst grows with growing acid concentrations.

The temperature coefficient can be calculated from the experiments of Table VI. The general composition of the solutions was: 3 cc. NaVO$_3$ + 5 cc. H$_2$C$_2$O$_4$ + x cc. 15 N H$_2$SO$_4$ + y cc. 4 N MnSO$_4$ + (12 − x − y) cc. H$_2$O. The temperature coefficient was constant, having a value of 3.2, and not changed in the presence of manganese ion.

TABLE VI

H$_2$SO$_4$ final concn. (N)	MnSO$_4$ final concn. (N)	$t_{1/2}^{20°}$ in minutes	$t_{1/2}^{30°}$ in minutes	t_{20}/t_{30}
0.75	..	199.5	60.75	3.28
3.75	..	282	86.25	3.27
3.75	1.0	56	18.25	3.07
			Average	3.22

4. Reduction of Vanadium Pentoxide with Formaldehyde.

—It is known that pentavalent vanadium is reduced by formaldehyde to the tetravalent state, but the reaction has not been studied before. From some preliminary experiments it has become clear that the reaction takes place only in concentrated acid solutions. (The reduction of vanadium pentoxide with hydrogen bromide is pronounced, also, only in solutions containing over 40% sulfuric acid.[2]) The steep rise in the velocity of the reaction was parallel to the appearance of an orange-red color in the acid vanadium pentoxide solutions.

Measurements in Acid Solutions.—The solutions contained: 3 cc. $^2/_3 M$ NaVO$_3$ + 1 cc. 40% H$_2$CO + x cc. acid; the total volume was 20 cc. The concentration of sulfuric acid varied be-
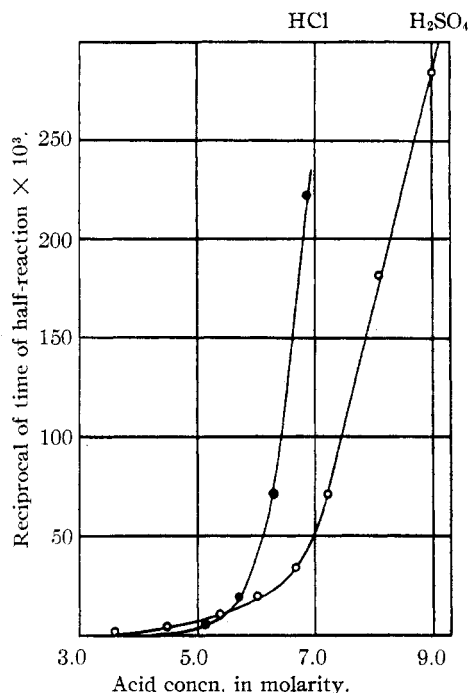

Fig. 4.—Rate of reduction of vanadium pentoxide by formaldehyde in acid solutions.

tween 1.8 to 9.0 M, while that of hydrochloric acid was between 5.15 to 6.87 M (for blank experiments with hydrochloric acid see section 3). The results are plotted in Fig. 4. The sulfuric acid curve shows that up to about 7 M sulfuric acid there was a slow rise in velocity, but from that point on there was a fast acceleration. In the solutions containing less than 4 M sulfuric acid the reaction was too slow to be measured. The hydrochloric acid curve was steeper, beginning at a concentration of about 5.5 M. Figure 5 shows
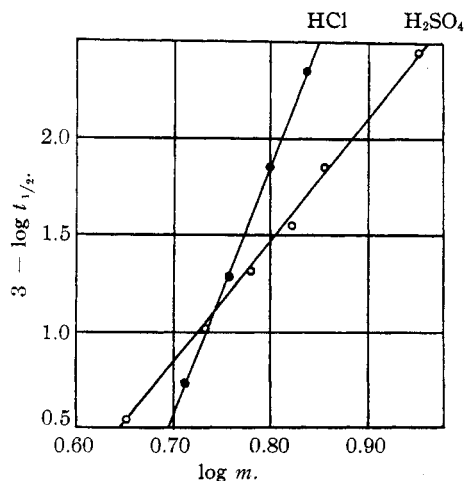

Fig. 5.—Rate of reduction of vanadium pentoxide by formaldehyde in acid solution.

the regular change in the reaction rate on increasing the acid concentration. Log $(t_{1/2}^{-1} \cdot 10^3)$ and log m ($m = M$ acid) are plotted on the ordinate and abscissa, respectively; in both cases we obtained straight lines.

The Order of Reaction.—Several series of experiments were made at constant concentrations of sulfuric acid and formaldehyde varying only the concentration of sodium vanadate. Table VII contains the results of two series of experiments. The time of half reaction was inversely proportional to the concentration of the vanadium. As the formaldehyde was present in the solutions in large excess, it can be concluded concerning the vanadium that the reaction is of the *second* order. Accordingly the second order equation $k = x/ta(a - x)$ was tried with good results in each case.

TABLE VII

NaVO₃ 2/3 M cc. (x)	6.66 M H₂SO₄		9.0 M H₂SO₄	
	$t_{1/2}$ min.	$t_{1/2} \times x$	$t_{1/2}$ min.	$t_{1/2} \times x$
2.0	37.8	75.6	5.4	10.8
4.0	18.5	74.0	2.65	10.6
6.0	12.75	76.5	1.9	11.4

Table VIII contains the results of a series of experiments with one or two cc. of formaldehyde 40% in sulfuric acid solutions of various concentration. (The solutions contained 3 cc. of sodium vanadate as usual.) As we see, the ratio t_1/t_2 decreases continuously with increase of sulfuric acid concentration until it reaches the value *one* at the concentration of 9 M sulfuric acid, while at about

4 M sulfuric acid it should have the value *two*. Accordingly the reaction is of the first order concerning the formaldehyde only in the lower acid concentrations, while at 9 M sulfuric acid the velocity of the reduction is independent of the formaldehyde concentration.

TABLE VIII

H₂SO₄ final concn. (M)	$t_{1/2}$ in minutes		t_1/t_2
	1 cc. H₂CO	2 cc. H₂CO	
5.40	97.0	57.0	1.70
6.66	29.5	20.75	1.42
7.20	14.0	10.5	1.33
9.00	3.5	3.75	0.93

The temperature coefficient was calculated from several experiments made at 30° and 20°; they differ in sulfuric acid (6–9 M) and hydrochloric acid (5 M) solutions and are equal to 1.6 and 2.4, respectively.

Influence of Cations.—Some experiments to accelerate the reaction were carried out with solutions composed as follows: 1 cc. ²/₃ M NaVO₃ + 0.5 cc. H₂CO 40% + 1 cc. additional electrolyte + 3 cc. concd. HCl (or 4.5 cc. concd. H₂SO₄) + H₂O. The total volume of each solution was 10 cc. The cations Ag⁺, Co⁺⁺, Mn⁺⁺, Fe⁺⁺⁺, Ni⁺⁺, Cd⁺⁺ and Cu⁺⁺ were studied in final concentrations varying from $N/250$ to $N/25$. None of these cations had a pronounced action; only Cu⁺⁺ accelerated the reaction slightly.

The nitrate ion had a special influence on the reduction of vanadium pentoxide with formaldehyde. (None of the other anions such as Br⁻, SO₃⁻⁻, CN⁻, CNS⁻, PO₄⁻⁻⁻, AsO₄⁻⁻⁻, exhibited this peculiar action.) For a quantitative study the following series of experiments was prepared: 3 cc. ²/₃ M NaVO₃ + 1 cc. H₂CO 40% + 9 cc. concd. HCl + x cc. $N/10$ HNO₃ + (7 − x) cc. H₂O. x varied from 0.5 to 4 cc. (The action of nitric acid in sulfuric acid solutions was similar to that in hydrochloric acid but was longer delayed; for this reason the hydrochloric acid solutions were preferred.) The results were not very well r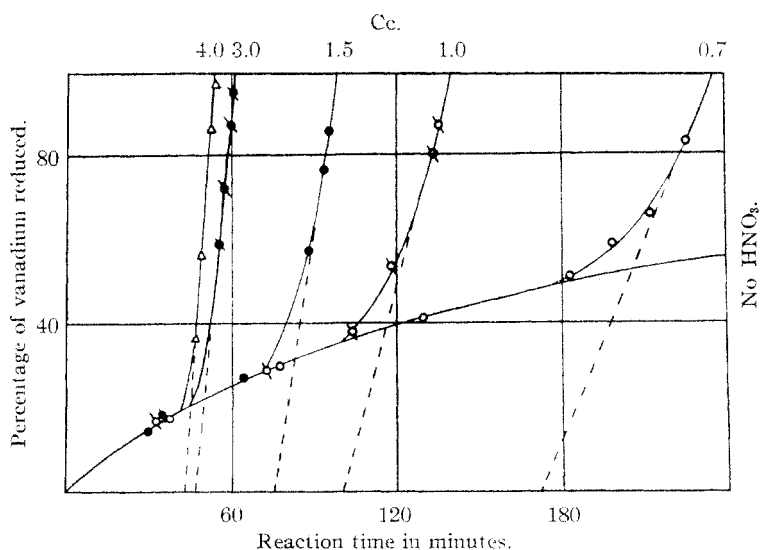eproducible unless the solutions were stirred very intensively for one minute during the addition of the last component (formaldehyde).

Figure 6 shows the course of reaction of the

Fig. 6.—Course of reduction of vanadium pentoxide by formaldehyde in presence of x cc. of 0.1 N nitric acid.

individual experiments (time of reaction against amount of vanadium reduced). Up to a definite time—the period of induction—depending on the amount of nitric acid present, no appreciable divergence from the course of the fundamental reaction (without nitric acid) was noted. Then suddenly the reaction was greatly accelerated and the solution turned blue in a very short time. The fully developed catalytic effect seemed to be linear. The period of induction also could be determined potentiometrically with great accuracy; using a platinum electrode there was a sudden drop of the potential corresponding to this point. If the time of induction (taken as the point of intersection between the fundamental curve and the catalytic straight line) is plotted against the concentration of nitric acid—a hyperbola is obtained (Fig. 7). The time of induction is therefore inversely proportional to the nitric acid concentration. From this curve it can be concluded also that a minimum amount of nitric acid (0.6 cc. $N/10$) is necessary in order that the induction should occur. Above 3 cc. of $N/10$ HNO$_3$ the influence of nitric acid is very small. The sensitivity of nitric acid appears to be greatest at a concentration where the ratio HNO$_3$/VO$_2^+$ is about 1 to 20. Some experiments were carried out at 20° and 30° in order to determine the influence of temperature on the time of induction. The *temperature coefficient* was equal to 2.4, *i. e.*, exactly the same value as obtained for the reaction in absence of nitric acid.

The influence of various cations on the nitric acid induction can be seen in Table IX. The general composition of the solutions was: 3 cc. $^2/_3 M$ NaVO$_3$ + 1 cc. 40% H$_2$CO + 9 cc. concd. HCl + 4 cc. $N/10$ HNO$_3$ + x cc. salt solution + $(3 - x)$ cc. H$_2$O. Ca^{++}, Mg^{++}, Cd^{++}, Ni^{++}, Al^{+++}, Cr^{+++} did not change the general character of the effect but reduced the time of induction somewhat below forty minutes; Zn^{++} and Co^{++} had no influence at all; Fe^{+++} lengthened the time of induction, while in the solutions containing Mn^{++} and Cu^{++} there was no visible effect even after many hours. (These cations also gave stable complexes with nitric oxide.) It was thought that nitrous acid might be a link in the catalytic reduction, as nitrous acid reduced acid solutions of pentavalent vanadium very quickly. A solution composed like the above was prepared, but instead of nitric acid, nitrous acid (= sodium nitrite) was introduced. The amount
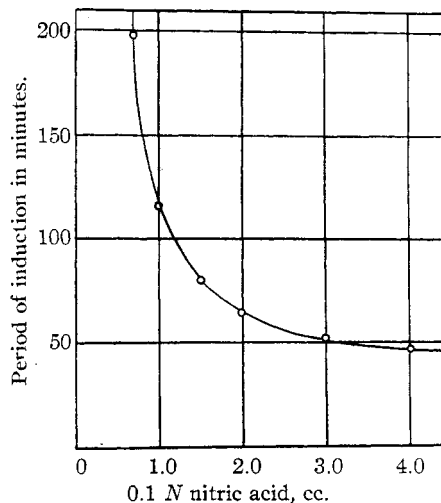

Fig. 7.—Induction of the reduction of vanadium pentoxide by formaldehyde in presence of nitric acid.

of nitrous acid was sufficient to reduce only one-fifth of the vanadium present. The whole amount of vanadium pentoxide was quickly reduced only after the passing of a period of time equal to the induction time, corresponding to an equivalent concentration of nitric acid. This experiment shows clearly that nitrous acid must be at first oxidized before induction can take place.

TABLE IX

Salt solution		Per cent. of V^{IV} after minutes				
Formula	final N	30	40	50	60	120
NiSO$_4$	0.05	17.4	55.5	95.1	....	....
CaCl$_2$	.10	17.0	55.0	94.3	....	....
Cr$_2$(SO$_4$)$_3$	.05	18.3	47.4	96.2	....	....
Al$_2$(SO$_4$)$_3$	.30	16.3	35.0	93.2	....	....
MgSO$_4$	.10	14.3	30.3	94.5	....	....
CdSO$_4$	.10	11.7	26.9	92.5	....	....
H$_2$O	...	16.5	20.6	57.3	97.5	....
ZnSO$_4$	.10	12.7	19.5	74.2	95.9	....
CoSO$_4$	.05	13.1	19.5	41.9	93.6	....
Fe$_2$(SO$_4$)$_3$	.10	13.1	17.4	18.7	22.2	93.0
MnSO$_4$	.10	16.9	18.3	21.9	24.7	38.3
CuSO$_4$	.05	14.9	19.4	21.7	32.1	(90)

5. Reduction of Vanadium Pentoxide with Ethyl Alcohol.—The reduction of vanadium pentoxide with ethyl alcohol is too slow to be measured at room temperatures, even in the presence of a big excess of alcohol and concentrated acid solutions; therefore the experiments were made at 50°. A cork with a pipet was fitted into each reaction flask, with the lower end of the pipet dipping into the solution. This pipet served to deliver fixed amounts of the solutions for measurements from time to time. The general composition of the solutions was: 3 cc. $^2/_3 M$ NaVO$_3$ + 2 cc. 96% C$_2$H$_5$OH (or 4 cc. alcohol) + x cc.
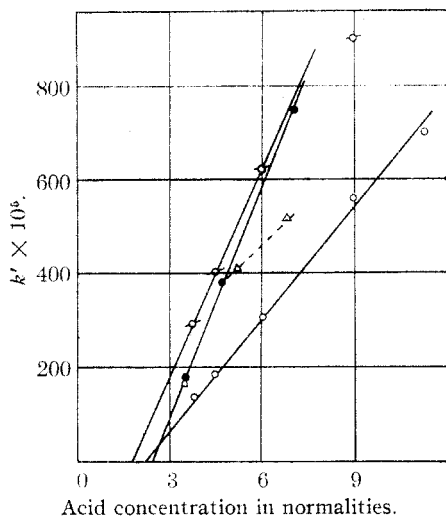
Fig. 8.—Rate of reduction of vanadium pentoxide by ethyl alcohol in acid solutions, at 50°: O, H_2SO_4 (2 cc. alc.); △, HCl; ●, $HClO_4$; ∅, H_2SO_4 (4 cc. alc.).

acid + H_2O; the total volume was 20 cc. The reaction course followed the first order formula: $k = 1/t \log a/(a - x)$. Good constants were obtained in all the solutions of lower acid concentration but in concentrated hydrochloric acid solutions there is a definite fall in the constants during the reaction (for blank experiments with hydrochloric acid see section 3). A similar but a less pronounced tendency of the constants to fall was noticed also in the most concentrated sulfuric acid and hydrochloric acid solutions. The results are plotted in Fig. 8. As is seen in the figure, the velocity of the reaction rises linearly with the acid concentration (with the exception of hydrochloric acid). Below the acid concentration of about two normal the reaction stops altogether. Sulfuric acid solutions which contained 4 cc. alcohol gave a line having an angle of inclination just double of that of the 2-cc. line. From this it can be concluded that the reaction is of the first order with reference to the alcohol as well.

The influence of concentrated alcoholic solution was studied in various acid solutions of about 3.5 N. Figure 9 shows that in all the acids used the velocity of the reaction was proportional to the concentration of alcohol. The straight lines indicate that the effect of the strong acids of a known normality was independent of the concentration of the alcohol.

The temperature coefficient of the vanadium pentoxide–alcohol reaction was 2.8, as calculated from the experiments of Table X. In the prepara-
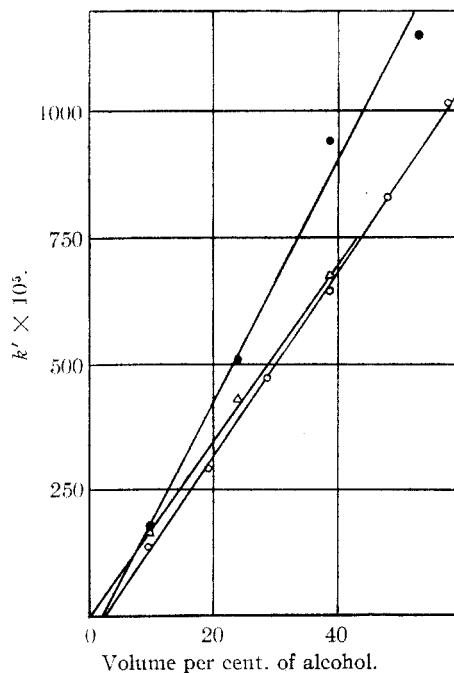

Fig. 9.—Rate of reduction of vanadium pentoxide by ethyl alcohol in acid solutions: O, H_2SO_4 3.75 N; △, HCl 3.44 N; ●, $HClO_4$ 3.50 N.

tion of these experiments an alcoholic solution of sulfuric acid was used. The final concentration of sulfuric acid in all these experiments was 3.75 N.

TABLE X

Volume % alcohol	k_{30°	k_{40°	k_{40}/k_{30}
40	0.000608	0.00166	2.73
55	.00101	.00285	2.82
65	.00135	.00385	2.83
75	.00160	.00441	2.76
		Average	2.78

Catalytic Agents.—Neither the cations tried nor phosphoric acid accelerated the reaction. Nitric acid showed a similar inductive action to the one recorded with formaldehyde, but far larger amounts of nitric acid had to be used.

General Conclusions

The velocity of reaction between pentavalent vanadium and four reducing agents: arsenious acid, oxalic acid, formaldehyde and alcohol, was studied. Strong acids accelerate the reaction in every case with the exception of oxalic acid. A comparison of the results obtained by us with the various reducing agents is given in Table XI. In Table XII the effects of various accelerators are compared; Mn^{++} and Fe^{+++} are specific catalysts

TABLE XI

Reducing agent	Lowest acid concn. (N) necessary for reaction H₂SO₄	HCl	Order of reaction concerning V^V	reducing agent	Temp. coeff. in H₂SO₄ solutions
As₂O₃	0.0	0.0	2	1	1.9
H₂C₂O₄	0.0	0.0	1	2	3.2
H₂CO	7.8	4.6	2	1-0	1.6
C₂H₅OH	2.0	2.0	1	1	2.8

TABLE XII

Reducing agent	Formula	Accelerator Upper and lower final concn. (N)	$t_{1/2}$ in minutes Without accel.	With accel. in max. concn.	Factor of acceleration
As₂O₃	H₃PO₄	0.0225-0.3	182	23	7.9
H₂C₂O₄	Mn⁺⁺	.25 −1.0	86.25	18.25	4.7
H₂C₂O₄	Fe⁺⁺⁺	.05 −0.5	86.25	440	0.2
H₂CO	HNO₃	.0025-0.02	186	46ᵃ	4.0
C₂H₅OH	HNO₃	.025 -0.25	485	32ᵃ	15.1

ᵃ The end of the induction period; from this point on the reaction passes very quickly.

for the oxidation of oxalic acid. The catalytic effect of phosphoric acid seems to be connected with the arsenious oxide and not with the vanadium. Nitric acid is a peculiar and very sensitive inductor in presence of formaldehyde and ethyl alcohol.

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The Activity Coefficients of Some Bivalent Metal Nitrates in Aqueous Solution at 25° from Isopiestic Vapor Pressure Measurements

BY R. A. ROBINSON, JEAN M. WILSON AND H. S. AYLING

In a recent communication[1] isopiestic measurements have been recorded from which the activity coefficient of calcium nitrate at 25° has been computed and found to be considerably lower than the activity coefficient of calcium chloride.[2] It is a matter of some interest, therefore, to obtain measurements on other nitrates of the alkaline earth metals and similar bivalent metals. We are now able to report results on magnesium, strontium, barium, cobalt, copper, cadmium and uranyl nitrate.

TABLE I

CONCENTRATIONS OF ISOPIESTIC SOLUTIONS OF POTASSIUM CHLORIDE AND BIVALENT METAL NITRATES AT 25°

Magnesium Nitrate

Molality Mg(NO₃)₂	KCl	Molality Mg(NO₃)₂	KCl	Molality Mg(NO₃)₂	KCl
0.1322	0.1865	0.5498	0.8746	1.585	3.144
.1347	.1899	.5659	.9118	1.631	3.262
.1430	.2006	.6681	1.099	1.662	3.362
.1605	.2265	.8318	1.419	1.757	3.600
.1739	.2490	1.043	1.871	2.040	4.371
.2931	.4317	1.294	2.442	2.065	4.439
.3517	.5344	1.474	2.885	2.120	4.609
.4197	.6440	1.583	3.145	2.197	4.831

Strontium Nitrate

Sr(NO₃)₂	KCl	Sr(NO₃)₂	KCl	Sr(NO₃)₂	KCl
0.08822	0.1184	0.4522	0.5870	1.872	2.319
.09650	.1290	.7331	.9330	1.921	2.356
.09980	.1330	.7574	.9666	2.206	2.712
.1205	.1591	.9450	1.199	2.446	3.014
.1443	.1898	1.264	1.582	2.811	3.456
.2069	.2723	1.363	1.700	2.974	3.658
.3125	.4088	1.565	1.952	3.498	4.314
.4496	.5820	1.795	2.210	3.909	4.843

(1) R. A. Robinson, THIS JOURNAL, 62, 3130 (1940).
(2) R. A. Robinson, Trans. Faraday Soc., 36, 735 (1940).

Barium Nitrate

Ba(NO₃)₂	KCl	Ba(NO₃)₂	KCl	Ba(NO₃)₂	KCl
0.09144	0.1151	0.1450	0.1775	0.3316	0.3743
.09208	.1155	.2184	.2591	.3598	.4030
.1194	.1489	.2240	.2664	.3961	.4358
.1413	.1735	.2899	.3322	.4022	.4434

Cobalt Nitrate

Co(NO₃)₂	KCl	Co(NO₃)₂	KCl	Co(NO₃)₂	KCl
0.1022	0.1419	1.137	2.009	1.760	3.454
.2297	.3293	1.155	2.038	1.815	3.587
.2932	.4263	1.214	2.177	1.886	3.772
.3715	.5498	1.223	2.203	1.935	3.898
.5798	.9028	1.362	2.499	1.990	4.033
.5962	.9322	1.421	2.640	2.198	4.578
.8645	1.445	1.477	2.767	2.244	4.678
.8881	1.490	1.487	2.810	2.261	4.738
1.109	1.948	1.650	3.178		

Copper Nitrate

Cu(NO₃)₂	KCl	Cu(NO₃)₂	KCl	Cu(NO₃)₂	KCl
0.1091	0.1514	0.4241	0.6132	1.618	2.936
.1211	.1820	.5389	.8181	1.701	3.136
.1921	.2691	.7310	1.150	1.915	3.633
.2333	.3300	1.000	1.668	2.158	4.178
.2382	.3383	1.183	2.032	2.283	4.501
.2585	.3684	1.390	2.442	2.415	4.828
.3060	.4411	1.529	2.766		

Cadmium Nitrate

Cd(NO₃)₂	KCl	Cd(NO₃)₂	KCl	Cd(NO₃)₂	KCl
0.1134	0.1571	0.6730	1.031	1.841	3.201
.1217	.1707	0.6863	1.048	1.873	3.255
.1559	.2190	1.041	1.672	1.989	3.497
.1975	.2778	1.138	1.848	2.162	3.824
.3309	.4766	1.206	1.974	2.315	4.150
.4141	.5061	1.267	2.082	2.381	4.269
.5345	.8012	1.531	2.597	2.638	4.810
.6409	.9786	1.681	2.888		