

A Kinetic Study of the Reduction of Vanadium(V) by Hydrazine in Strongly Acid Aqueous Solutions

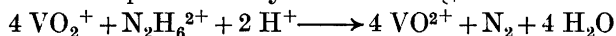
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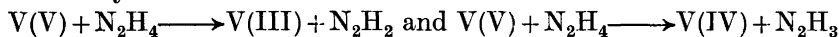
The kinetics of the reaction between vanadium(V) and hydrazine has been studied in strongly acid perchloric acid solutions with the ionic strength 1.00 M at 15, 20, 25, 30, and 35°C. The rate law obtained indicates a reaction mechanism with the reversible formation of a complex between vanadium and hydrazine as the first stage, followed by the reaction between this complex and vanadium(V). The nature of the complex is still uncertain and so are the products of the second reaction. The ultimate products are vanadium(IV) and nitrogen gas.

One rate constant and the ratio between two other rate constants, based on the proposed reaction mechanism, have been evaluated. The corresponding activation parameters have also been determined.

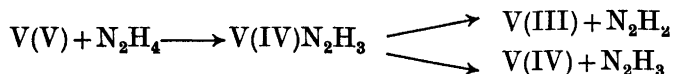
The aim of the present study is to elucidate the mechanism of the reaction between vanadium(V) and hydrazine in strongly acid aqueous solutions. This reaction can be represented by the following formula:



No kinetic studies on this reaction seem to have been carried out before. Kirk and Browne^{1,2} have discussed this reaction as regards the products formed under different experimental conditions. The main products are nitrogen and vanadium(IV), but minor amounts of ammonia, and at greater temperatures in strongly acid solutions hydroazoic acid, also appear. Higginson *et al.*^{3,4} have repeated these studies and also used ¹⁵N as a tracer to see whether the two nitrogen atoms of the nitrogen gas formed come from the same hydrazine molecule. These authors suggest two alternative reaction mechanisms which can explain the formation of ammonia as a by-product: (1) Two distinct reactions occur between vanadium(V) and hydrazine. These can be represented by the schematic formulae:



The first of these dominates and gives as the sole product nitrogen gas. Ammonia is formed by the reactions: $2 \text{N}_2\text{H}_3 \longrightarrow \text{N}_4\text{H}_6 \longrightarrow 2 \text{NH}_3 + \text{N}_2$. (2) There is a two-stage mechanism which may be written as follows:



Ammonia is formed by the reaction mentioned above.

The results of the present study indicate a two-stage mechanism with the formation of a complex between vanadium and hydrazine followed by a reaction between this complex and vanadium(V).

EXPERIMENTAL

Reagents. Vanadium(V) stock solutions were prepared by dissolving weighed amounts of vanadium pentoxide (containing more than 99.9 % V_2O_5) in 1.00 M perchloric acid. A couple of vanadium(V) stock solutions in 0.100 M HClO_4 + 0.90 M NaClO_4 were prepared by dissolving V_2O_5 in 1.00 M sodium hydroxide and then acidifying by addition of 1.00 M perchloric acid. This procedure was used because the dissolution of V_2O_5 in 0.1 M HClO_4 proceeds very slowly. The concentration of V(V) in the solutions was calculated from the weight of V_2O_5 .

Hydrazine stock solutions were prepared by dissolving weighed amounts of hydrazinium sulphate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$) in HClO_4 and/or NaClO_4 . The concentration of hydrazine was checked by titration with potassium iodate, according to Andrews.⁵ The hydrazine solutions were generally used up within a few days, and checks of the concentration did not show any noticeable decrease.

Vanadium(IV) solutions were prepared from vanadium(IV) oxide sulphate ($\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$). The concentration of V(IV) was checked spectrophotometrically.

Sodium perchlorate was used to keep the ionic strength constant at 1.00 M. All the chemicals used were of analytical grade.

Procedure. The measurements were carried out manually by a Zeiss PMQ II Spektral-photometer. The kinetic measurements were generally carried out at the wave length 340 nm, but a few measurements were carried out at 760 nm to verify that V(IV) was formed at the same rate as V(V) disappeared. The reaction was started by mixing the reagents either by pipette or by means of an all-glass syringe equipped with a device to allow the exhaustion of a well-defined volume of the reagent solution. The mixing with pipette was used for slow reactions, *i.e.* at low initial concentrations of the reactants whereas the mixing with syringe was used, when the reaction was rapid and it was essential to begin the measurements as fast as possible after the mixing. By the latter procedure it was possible to achieve complete mixing within a few seconds (in the absorption cell). The reagent solutions were thermostated before mixing, and so was the cell compartment of the spectrophotometer. The room was thermostated to within 2°C from the temperature at which the measurements were carried out (except at 15°C where the difference was 3°C).

SYMBOLS AND NOTATIONS

$[\text{V(V)}]$	over-all concentration of vanadium(V) (within the hydrogen ion concentration range used = $[\text{VO}_2^+]$ ⁶).
$[\text{N}_2\text{H}_4]$	over-all concentration of hydrazine.
$[\text{V(IV)}]$	over-all concentration of vanadium(IV).
$[\text{V(V)}]_0$	over-all concentration of vanadium(V) at the time $t=0$ after mixing.
$[\text{N}_2\text{H}_4]_0$	over-all concentration of hydrazine at the time $t=0$ after mixing.
A	absorbance.
a	linear absorption coefficient ($a = A/l$; l = path length).
a_0	linear absorption coefficient at the time $t=0$ after mixing.
a_∞	linear absorption coefficient at complete reaction ($t = \infty$).

ϵ	molar absorption coefficient ($\epsilon = A/l c$; c = concentration).
λ	wave length.
n	number of measurements.
s	standard deviation.

MEASUREMENTS, CALCULATIONS AND RESULTS

Preliminary studies. In order to establish the nature of the resulting vanadium species, the vanadium(V) solution was mixed with a two-fold excess of hydrazine; and the absorption curve within the wave length range 320–850 nm was determined after the reaction had ceased. This absorption curve is identical with the one obtained for VO^{2+} under the same experimental conditions (1.00 M HClO_4). The absorption curve of V(V) in 1.00 M HClO_4 was determined within the same wave length range. The fact that the absorption curve of V(V) does not have any noticeable absorption until below about 400 nm where the curve rises steeply made necessary special precautions in the setting of the wave length scale on the spectrophotometer in the subsequent measurement at a constant wave length. Every time a new setting was made the molar absorption coefficient of V(V) was checked. The wave length 340 nm was chosen for the kinetic measurements. At this wave length, $\epsilon_{\text{V(IV)}}$ is only about 1 % of $\epsilon_{\text{V(V)}}$.

The validity of Lambert-Beer's law was established at 340 nm for $[\text{V(V)}] = 0 - 12$ mM. A was found to be proportional to $[\text{V(V)}]$ within the whole concentration range. $\epsilon_{\text{V(V)}} = 201.4 \pm 1.2 \text{ M}^{-1} \text{ cm}^{-1}$. This value was calculated from the obtained absorbances by a Hewlett-Packard desk top computer using a least squares program designed for the calculation of the slope and intercept of a straight line. The error limits given throughout this paper represent three standard deviations.

The fact that previous studies have shown that ammonia appears as a by-product of the reaction necessitated an investigation of the stoichiometry. A series of solutions was prepared having the same $[\text{V(V)}]_0$ but different $[\text{N}_2\text{H}_4]_0$. In one of these solutions hydrazine was exchanged for an excess of sodium sulphite. The solutions were kept at 25.00°C and the absorbances at 340 nm and 760 nm (the absorption maximum of V(IV)) were measured

Table 1. Determination of the stoichiometry. $[\text{V(V)}]_0 = 10.00$ mM; 25.00°C.

$[\text{N}_2\text{H}_4]_0$ mM	$\lambda = 340$ nm		$\lambda = 760$ nm	
	a_∞	$\frac{\text{mol V(V)}}{\text{mol N}_2\text{H}_4}$	$4a_\infty$	$\frac{\text{mol V(V)}}{\text{mol N}_2\text{H}_4}$
0	2.017	—	0.006	—
1.00	1.215	4.02	0.273	3.99
1.50	0.820	4.00	0.407	4.00
2.00	0.429	3.98	0.537	3.97
2.50	0.056	3.93	0.663	3.93
10.00	0.020	—	0.676	—
Na_2SO_3	0.022	—	0.673	—

every third day, until they remained unchanged between two successive measurements. This condition was attained already after three days. The results (which represent the mean values of two parallel series) are shown in Table 1 together with the calculated number of mol V(V) consumed per mol N_2H_4 . The obtained values lie close to the values expected if no side reaction(s) occur(s). For stoichiometric proportions of the reactants this value lies significantly below. This is, however, so small a decrease that the side reaction(s) can be neglected in the following treatment.

Determination of the rate law at a constant hydrogen ion concentration.

The determination of the dependence of the reaction rate on $[V(V)]$, $[V(IV)]$ and $[N_2H_4]$ was performed at a constant hydrogen ion concentration (1.00 M $HClO_4$) at the temperature $25.00 \pm 0.05^\circ C$.

The initial rates $-(da/dt)_0 \approx -(\Delta a/\Delta t)_0$ were determined for solution having a constant $[V(V)]_0 (=2.00 \text{ mM})$ while $[N_2H_4]_0$ was changed, and for solutions having a constant $[N_2H_4]_0 (=1.00 \text{ mM})$ while $[V(V)]_0$ was changed. The results are shown in Figs. 1 and 2. The reaction rate is proportional to

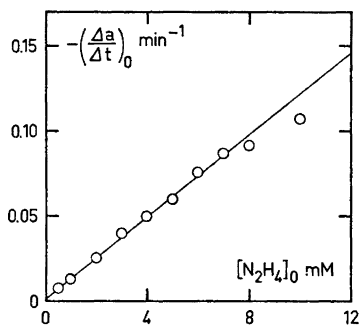


Fig. 1. The initial reaction rate $-(\Delta a/\Delta t)_0$ versus $[N_2H_4]_0$. $[V(V)]_0 = 2.00 \text{ mM}$; $25.00^\circ C$; $\lambda = 340 \text{ nm}$.

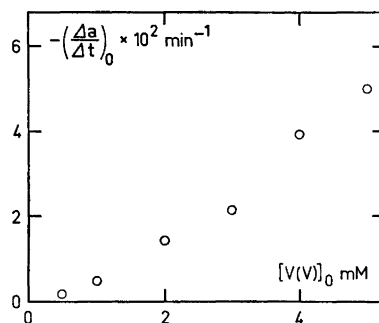


Fig. 2. The initial reaction rate $-(\Delta a/\Delta t)_0$ versus $[V(V)]_0$. $[N_2H_4]_0 = 1.00 \text{ mM}$; $25.00^\circ C$; $\lambda = 340 \text{ nm}$.

$[N_2H_4]_0$ for $[N_2H_4]_0 < 7 \text{ mM}$. The deviations from the proportionality at greater $[N_2H_4]_0$ values is probably due to the fact that the error introduced by putting $-(da/dt)_0 = -(\Delta a/\Delta t)_0$ becomes greater the more rapid the reaction is. The dependence of the reaction rate on $[V(V)]_0$ is more complicated (cf. Fig. 2). The precision of the determined initial rates makes them less suited for the determination of the exact dependence of the reaction rate on $[V(V)]$. Since, however, the reaction rate is proportional to $[N_2H_4]$ another procedure, yielding more precise values of the reaction rates, can be used. If the initial concentrations of V(V) and N_2H_4 are such that $[V(V)]_0 = 4[N_2H_4]_0$, the ratio of the two concentrations will remain unchanged throughout the reaction. Therefore, the dependence of the reaction rate on $[V(V)]$ can, in principle, be determined from one kinetic run with the reactants present in stoichiometric proportions. The slope of the a versus t curve is determined at certain values of a (corresponding to different values of $[V(V)]$) and divided by $[V(V)]/4$. The

values obtained then are the reaction rates ($-da/dt$) at the $[V(V)]$ in question and a definite value of $[N_2H_4]$ ($=1$ M). In order to improve the precision several runs were made. Instead of determining the reaction rate from a as a function of t , $1/a$ as a function of t , which has a more gentle curvature, was used. Since $-da/dt = a^2 (d(1/a)/dt)$, the reaction rates could readily be calculated. $\Delta(1/a)/\Delta t$ around certain a -values was determined graphically. It was found that the order with regard to $V(V)$ lay between 1 and 2, decreasing with increasing $[V(V)]$. It therefore seemed likely that the rate law was of the form

$$-\frac{d[V(V)]}{dt} = \frac{k[N_2H_4][V(V)]^2}{1 + k'[V(V)]} \quad (1)$$

which would give the obtained order.

In order to study the effect of the reaction product $V(IV)$ on the reaction rate $VOSO_4$ was added to the $V(V)$ solution. In the presence of 50 mM $VOSO_4$ the rate increased about 20 %. The same effect was, however, observed, when 50 mM Na_2SO_4 was added to the $V(V)$ solution instead. The increase therefore seems to be due to the rather great concentration of sulphate ions added together with the VO^{2+} ions.

Eqn. (1) can be rewritten as

$$-\frac{da}{\varepsilon_{V(V)} dt} = \frac{k[N_2H_4][V(V)]^2}{1 + k'[V(V)]} \quad (2)$$

which can be rearranged to

$$-\frac{[N_2H_4][V(V)]}{da/dt} = \frac{k'}{\varepsilon_{V(V)}k} + \frac{1}{k[V(V)]\varepsilon_{V(V)}} \quad (3)$$

or approximately

$$-\frac{[N_2H_4][V(V)]}{\Delta a/\Delta t} = \frac{k'}{\varepsilon_{V(V)}k} + \frac{1}{k[V(V)]\varepsilon_{V(V)}} \quad (4)$$

The proposed rate law can be verified by plotting $-[N_2H_4][V(V)]/(\Delta a/\Delta t)$ versus $1/[V(V)]$. If it is the right one a straight line should be obtained with the intercept $k'/\varepsilon_{V(V)}k$ and the slope $1/k\varepsilon_{V(V)}$. That this is so can be seen from Fig. 3. Every point in this figure represents the mean value of 5–13 determinations. The corresponding values are shown in Table 2. In order to evaluate the constants k and k' , a least squares program was used. All the experimental values (except those at $[V(V)] < 1.5$ mM, which were too unreliable) were used in this calculation. The following values were obtained: $k = 522 \pm 58 \text{ M}^{-2} \text{ s}^{-1}$; $k' = 404 \pm 45 \text{ M}^{-1}$. The full drawn line in Fig. 3, marked 25°C, has been calculated using these values.

The obtained rate law can be integrated and gives for stoichiometric proportions of $V(V)$ and N_2H_4 the expression

$$\frac{1}{t} \left(\frac{1}{[V(V)]^2} - \frac{1}{[V(V)]_0^2} \right) = \frac{k}{2} - 2k' \frac{1}{t} \left(\frac{1}{[V(V)]} - \frac{1}{[V(V)]_0} \right) \quad (5)$$

which can be rewritten as

Table 2. The reaction rate $-\Delta a/\Delta t$ at different $[V(V)]$. $[V(V)] = 4 [N_2H_4]$; $25.00^\circ C$; $\lambda = 340$ nm; $l = 1$ cm.

$[V(V)]$ mM	$-(\Delta a/\Delta t) \times 10^3 \text{ min}^{-1}$	$s \times 10^3$	n
1.00	1.155	0.057	5
1.25	2.123	0.045	6
1.50	3.311	0.053	7
1.75	4.973	0.056	8
2.00	6.99	0.10	8
2.25	9.25	0.14	7
2.50	12.25	0.12	13
3.00	19.39	0.24	10
4.00	39.91	0.77	11
5.00	63.35	0.41	11
6.00	98.50	0.74	11
7.00	141.4	0.9	10
8.00	193.8	2.6	8

$$Y = \frac{k}{2} - 2k'X \quad (6)$$

If the proposed rate law is correct, a plot of Y versus X should give a straight line with the intercept $k/2$ and the slope $2k'$. All the measurements should fit the same straight line. Fig. 4 shows the corresponding plot for one kinetic run (for the sake of clarity only about 10 % of the experimental values are shown). It is seen that the points can be accommodated to a straight line thus verifying the proposed rate law. The random experimental errors influence to a great extent the values of X and Y in the beginning and in the end of

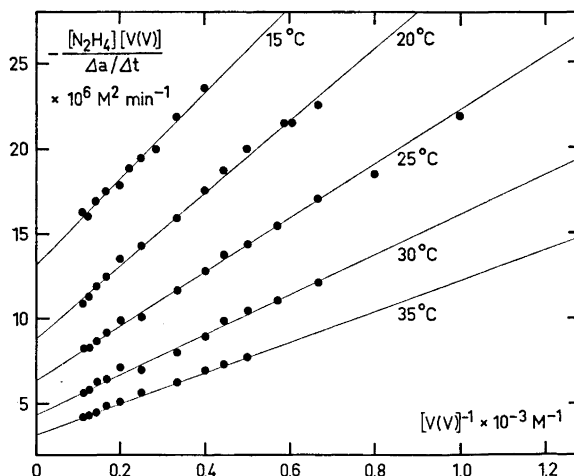


Fig. 3. $-[N_2H_4][V(V)]/(\Delta a/\Delta t)$ versus $1/[V(V)]$. $[V(V)] = 4 [N_2H_4]$; $\lambda = 340$ nm.

the run. This makes the available X-range rather narrow. The constants k and k' were calculated by this procedure for nine kinetic runs which were extended over a sufficiently long time to give a reasonable change of X. The following mean values were obtained: $k = 519 \pm 37 \text{ M}^{-2}\text{s}^{-1}$; $k' = 384 \pm 32 \text{ M}^{-1}$. These values should be compared with the corresponding values obtained by applying eqn. (4) to the same kinetic runs and by calculating the mean values of the obtained constants: $k = 522 \pm 34 \text{ M}^{-2}\text{s}^{-1}$; $k' = 339 \pm 39 \text{ M}^{-1}$. There is an excellent agreement between the values obtained by the two methods and, furthermore, the error limits (three standard deviations) are approximately equal.

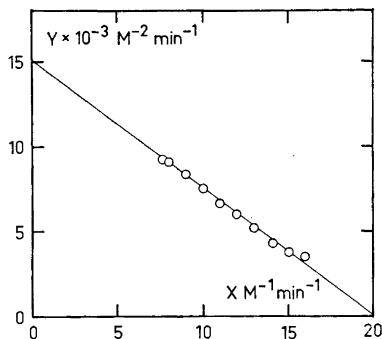


Fig. 4. The quantity Y versus X for one kinetic run. 25.00°C. $[V(V)]_0 = 4[N_2H_4]_0$.

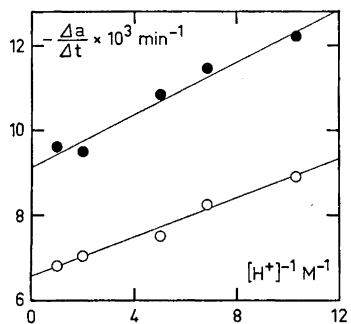


Fig. 5. $-\Delta a/\Delta t$ versus $1/[H^+]$ at 25.00°C (○) and 30.00°C (●). $[V(V)] = 2.00 \text{ mM}$; $[N_2H_4] = 0.50 \text{ mM}$; $\lambda = 340 \text{ nm}$.

Dependence on the hydrogen ion concentration. The rate law given above is valid only at a constant hydrogen ion concentration, viz. 1.00 M. In order to determine the effect of the hydrogen ion concentration, kinetic runs were made at constant values of $[V(V)]$ and $[N_2H_4]$ but at different values of $[H^+]$ (at 25.00 and 30.00°C). To increase the precision as far as possible, the procedure was standardized: equal volumes of thermostated 5.00 mM V(V) solution and 1.25 mM N_2H_4 solution with the proper hydrogen ion concentration were mixed by pipette in flasks, thoroughly shaken, and transferred to an absorption cell (path length = 3 cm). The absorbances were read every half minute until they had passed a value corresponding to $[V(V)] \approx 1.8 \text{ mM}$. The reaction rate at $[V(V)] = 2.00 \text{ mM}$ was evaluated in the manner described above. For every value of $[H^+]$, 2–3 runs were made. The reaction rate was found to be a linear function of $1/[H^+]$ (Fig. 5), and thus

$$k = k'' + \frac{k'''}{[H^+]} \quad (7)$$

The following values were obtained by the least squares procedure. 25°C: $k'' = 500 \pm 52 \text{ M}^{-2}\text{s}^{-1}$; $k''' = 17 \pm 4 \text{ M}^{-1}\text{s}^{-1}$; 30°C: $k'' = 663 \pm 125 \text{ M}^{-2}\text{s}^{-1}$; $k''' = 22 \pm 8 \text{ M}^{-1}\text{s}^{-1}$.

Since k''' is only small, it might be suspected to be a spurious constant caused by the exchange of H^+ for Na^+ . If this is so, the exchange of Na^+ for

Li^+ should cause a similar effect. Therefore, the described procedure was repeated at 25.00°C, but this time, $[\text{H}^+]$ was kept constant (0.500 M), while Na^+ was replaced by Li^+ . The results of this study are shown in Table 3. The

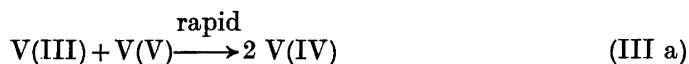
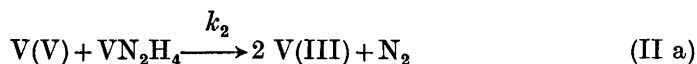
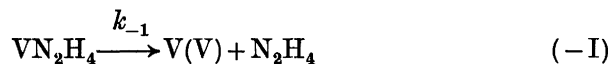
Table 3. The reaction rates $-\Delta a/\Delta t$ at different $[\text{Na}^+]$ and $[\text{Li}^+]$. $[\text{V}(\text{V})]=2.00$ mM; $[\text{N}_2\text{H}_4]=0.50$ mM; $[\text{H}^+]=0.500$ M; $\lambda=340$ nm; 25.00°C.

$[\text{Na}^+]$ M	$[\text{Li}^+]$ M	$-(\Delta a/\Delta t) \times 10^3 \text{ min}^{-1}$
0.500	0	6.93 ± 0.12
0.400	0.100	7.11 ± 0.72
0.250	0.250	7.05 ± 0.10
0	0.500	7.36 ± 0.09

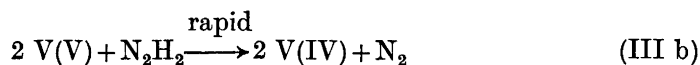
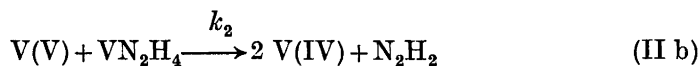
reaction rates were within the experimental error the same, irrespective of the proportion between Na^+ and Li^+ . The constant k''' therefore seems to be genuine.

DISCUSSION

The rate law determined above indicates a rate-determining two-stage mechanism with a reversible formation of a complex between vanadium and hydrazine as the first step. This is followed by a reaction between the complex and "free" vanadium(V). The nature of the complex formed in the first step is very uncertain. There might be three possibilities differing in the oxidation state of vanadium and hydrazine, *viz.* $\text{V}(\text{V})\text{N}_2\text{H}_4$, $\text{V}(\text{IV})\text{N}_2\text{H}_3$, and $\text{V}(\text{III})\text{N}_2\text{H}_2$. These formulae merely represent the oxidation states and not the detailed structure of the species. The fact that the back reaction of the complex formation manifests itself in the rate law might indicate the formation of the complex without any change of the oxidation states. As far as the rate law is concerned, two mechanisms having the same general features can be proposed.



and



By applying the steady state approximation as regards the complex VN_2H_4 , the following rate law is obtained

$$-\frac{d[\text{V(V)}]}{dt} = \frac{4 k_1 k_2 [\text{N}_2\text{H}_4] [\text{V(V)}]^2}{k_{-1} + k_2 [\text{V(V)}]} \quad (8)$$

which is analogous to the experimentally obtained one.

Browne and Shetterly² have detected V(III) by means of silver sulphate in the reaction mixture, when hydroazoic acid is formed as a by-product. When no hydroazoic acid was formed, these authors could not prove the formation of V(III). In the present study, no reduction of silver sulphate could be observed, even at elevated temperatures.

Assuming eqn. (8) to be valid, the rate constant k_1 and the ratio of rate constants k_{-1}/k_2 can be evaluated from the experimental values given in Table 2 and Fig. 2. The following values are obtained:

$$k_1 = 0.323 \pm 0.017 \text{ M}^{-1} \text{ s}^{-1}; k_{-1}/k_2 = (2.48 \pm 0.27) \times 10^{-3} \text{ M}$$

The dependence of the reaction rate on $[\text{H}^+]$ indicates two parallel reactions corresponding to reaction (I) and for which the corresponding transition complexes differ in the number of bound hydrogen ions. Hydrazine is the only reactant that is likely to lose or take up hydrogen ions within the studied hydrogen ion concentration range (0.1–1.0 M).⁶ It therefore seems reasonable to believe that the two parallel reactions involve the two ions $\text{N}_2\text{H}_6^{2+}$ and N_2H_5^+ . The former of these reactions dominates, and in 1.00 M HClO_2 , the latter reaction can be neglected ($k''' \ll k''$).

ACTIVATION PARAMETERS

The determination of k_1 and k_{-1}/k_2 , outlined above, has been repeated at 15, 20, 30, and 35°C in order to evaluate the activation parameters. The results are summarized in Table 4. Fig. 3 shows $-\text{[N}_2\text{H}_4][\text{V(V)}]/(\Delta a/\Delta t)$ versus $1/[\text{V(V)}]$ also at these temperatures.

The Arrhenius activation energy E_1 of reaction (I) and the difference between the corresponding activation energies of reaction (–I) (E_{-1}) and (II) (E_2) were calculated by the method of least squares using the equations

Table 4. The rate constant k_1 and the ratio of rate constants k_{-1}/k_2 at different temperatures.

Temp.°C	$k_1 \text{ M}^{-1}\text{s}^{-1}$	$(k_{-1}/k_2) \times 10^3 \text{ M}$
15.00	0.157 ± 0.025	1.90 ± 1.02
20.00	0.234 ± 0.008	2.41 ± 0.18
25.00	0.323 ± 0.017	2.48 ± 0.27
30.00	0.474 ± 0.040	2.71 ± 0.47
35.00	0.649 ± 0.030	2.90 ± 0.30

$$\ln k_1 = \ln Z_1 - \frac{E_1}{RT} \quad (9)$$

$$\ln \frac{k_{-1}}{k} = \ln \frac{Z_{-1}}{Z_2} - \frac{E_{-1} - E_2}{RT} \quad (10)$$

where Z denotes the frequency factors.

According to the transition state theory, the temperature dependence of a rate constant is given by the equation

$$\ln k_1 = \ln \frac{k_b T}{h} + \frac{\Delta S_1^\ddagger}{R} - \frac{\Delta H_1^\ddagger}{RT} \quad (11)$$

k_1 = rate constant; k_b = Boltzmann's constant; h = Planck's constant; ΔH_1^\ddagger = activation enthalpy; ΔS_1^\ddagger = activation entropy.

The activation enthalpy can be calculated from the Arrhenius activation energy by the relation

$$\Delta H_1^\ddagger = E_1 - RT \quad (12)$$

The following values were obtained: $E_1 = 51.7 \pm 3.2$ kJ/mol; $E_{-1} - E_2 = \Delta H_{-1}^\ddagger - \Delta H_2^\ddagger = 14.2 \pm 8.0$ kJ/mol; $\ln Z_1 = 19.76 \pm 1.29$; $\Delta H_1^\ddagger = 49.2 \pm 3.2$ kJ/mol; $\Delta S_1^\ddagger = -89 \pm 11$ J/mol K; $\Delta S_{-1}^\ddagger - \Delta S_2^\ddagger = -247 \pm 29$ J/mol K.

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