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THE THERMAL OXIDATION OF HYDRAZINE MONOHYDRATE IN THE VAPOR PHASE

by

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Purdue Research Foundation
and
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SUMMARY

1. The vapor pressure of hydrazine monohydrate has been determined over the temperature range from 27.6°C to 120°C. The vapor pressure of hydrazine monohydrate is lower than that of pure hydrazine or pure water at the same temperature. The vapor pressure can be determined from the following equation with an accuracy of about plus or minus 2 per cent.

$$\log_{10} P = 0.3389 - \frac{752.5}{T} + 0.01138T$$

2. The experimental data obtained in this investigation indicate that hydrazine monohydrate completely dissociates in the vapor phase into hydrazine, N_2H_4, and water vapor over the temperature range from 71.2°C. to 151.2°C.

3. The thermal oxidation of hydrazine monohydrate by oxygen was studied in a constant volume reactor constructed of pyrex glass. The experiments were carried out under isothermal conditions and with various concentrations of hydrazine, oxygen, water vapor, and nitrogen. A series of runs was made with each one of these components present in a large excess in the reacting mixture.

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INTRODUCTION

The consideration of hydrazine monohydrate as a fuel for rocket and jet engines has stimulated interest in the method by which it reacts with oxygen. In connection with the investigation from a broader viewpoint of the reaction under explosive conditions, a study of the thermal oxidation of hydrazine monohydrate by oxygen under conditions of slow combustion was instigated.

In any reaction which proceeds at a rate such that time may be considered a measurable variable, there is considerable utility in being able to express, in one form or another, the progress of the reaction as a function of time. Such an expression provides a common basis for comparing the effects of various conditions upon the rate of the reaction. The usual method of obtaining such an expression is by proposing that the rate of reaction is proportional to some power of the concentration of each of the reactants. After the respective exponents have been properly determined on the basis of experimental data, the differential rate equation is integrated to a form which expresses degree of completion of the reaction as a function of time.

In the course of this investigation, data were obtained for the thermal oxidation of hydrazine monohydrate in a pyrex glass reactor of constant volume. An attempt was made to derive an expression which relates the progress of the reaction to time in the form of an integral order reaction rate equation.

EXPERIMENTAL INVESTIGATION

Apparatus. The apparatus for the thermal oxidation of hydrazine monohydrate consisted of a pyrex glass reactor surrounded by a jacket through which oil was circulated from a thermostatically controlled heating tank. A schematic diagram of the equipment is shown in Figure 1 and a photograph, Figure 2, is also included. Pressures within the reactor were read by means of a manometric system which also served the purpose of maintaining constant volume within the

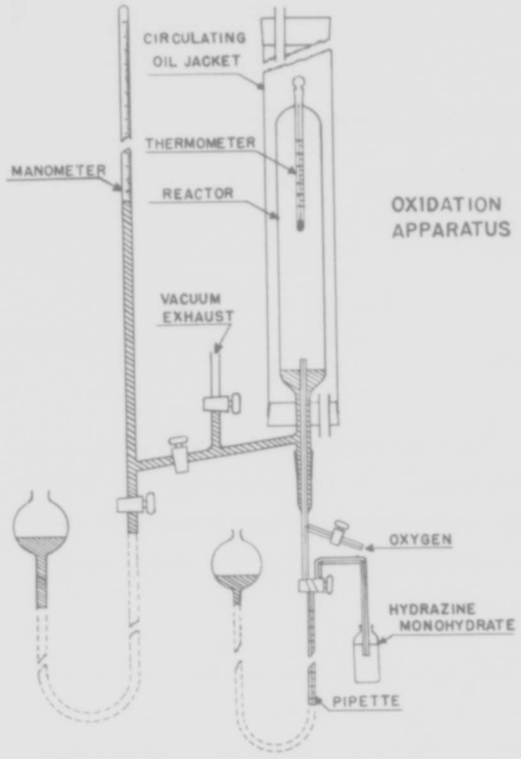

Fig. 1. Schematic diagram of equipment.

reactor. The reactor was designed so that only mercury and glass were in contact with the reactants and so that there was no dead space. The temperature of the reactants within the reactor was read from a thermometer suspended within the reactor by means of a ground glass joint. The hydrazine monohydrate was charged to the reactor by positive displacement with mercury from a pipette which extended into the reactor above the mercury seal maintained in the bottom of the reactor. The mercury seal was maintained at this point to prevent any reaction in lines connected to the bottom of the reactor. The pipette was extended above the mercury seal to prevent occlusion of hydrazine monohydrate in the mercury seal when charging the reactor. Oxygen was also charged to the reactor through this pipette. Before each run was started, the entire reactor system was evacuated by means of a Megavac Pump. Leveling bulbs were employed to add and withdraw mercury from the reactor. The thermometer employed to measure the temperature within the reactor and the temperature within the jacket were calibrated against a standard thermometer. During the experimental runs, the mercury seal in the bottom of the reactor was adjusted such that the volume of the reactor was 888 ml.

Vapor Pressure of Hydrazine Monohydrate. The vapor pressure of hydrazine monohydrate was determined over a range of temperatures from 27.6°C to 100°C so that conditions could be selected for carrying out the oxidation reaction in the vapor phase so as to prevent condensation of any portion of the hydrazine monohydrate charged to the reactor. The apparatus constructed for the thermal oxidation of hydrazine monohydrate was employed in obtaining vapor pressure data.

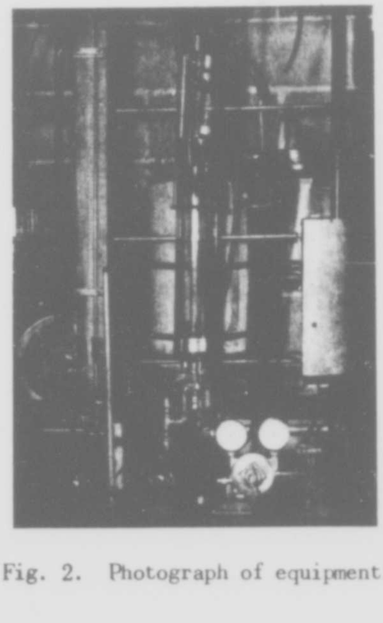

Fig. 2. Photograph of equipment.

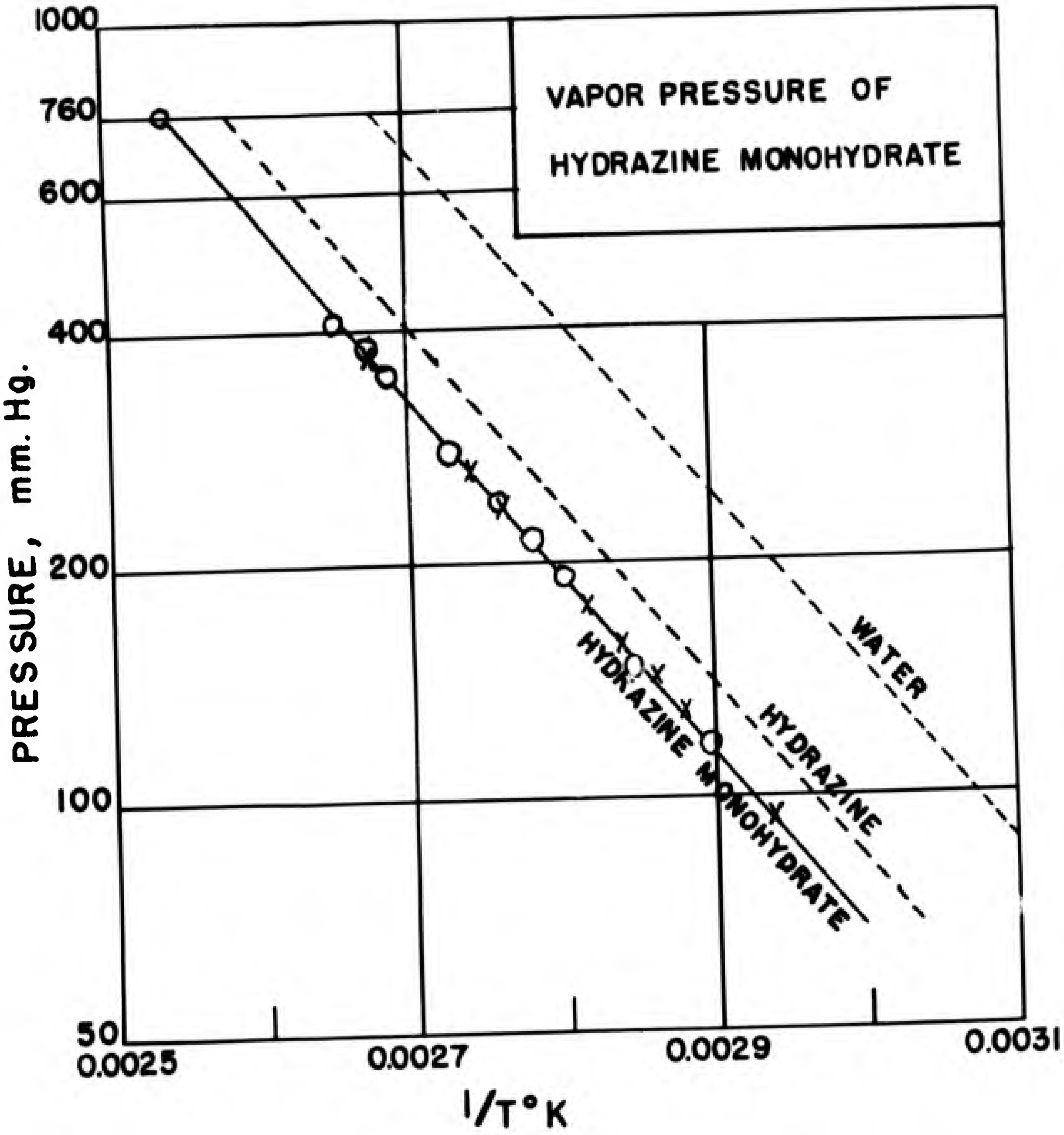

Fig. 3. Vapor pressure of hydrazine monohydrate.

The reactor was first evacuated to a pressure of 0.01 mm Hg and charged with about 1 ml of 100% hydrazine monohydrate. The reactor was then heated to a given temperature by means of the oil circulating through the surrounding jacket, and the thermo-regulator was then set to maintain this temperature. The system was allowed to come to thermal equilibrium before pressure readings were taken on the manometer. Necessary precautions were taken to insure that liquid hydrazine monohydrate was present in the reactor at all times.

The observed vapor pressure data are plotted in Figure 3 as a function of the reciprocal

Table 1. Vapor pressure of hydrazine monohydrate.

t $^{\circ}$C	P (observed) mm	P (calculated) mm.
27.6	19.	
45.4	33.8	
54.3	51.	
63.1	73.5	
67.2	94.	96.8
72.0	116.	118.
74.4	129.	130.
76.8	143.	143.
79.2	159.	158.
81.6	175.	174.
84.0	193.	191.
86.6	213.	212.
89.2	235.	234.
91.8	261.	259.
97.0	318.	318.
99.0	343.	343.
101.0	369.	370.
120.0	760.	758.

of the absolute temperature in degrees Kelvin. The vapor pressures of pure water and pure hydrazine are plotted on the same graph for the purpose of comparison. The vapor pressure of hydrazine monohydrate in the range from a pressure of 100 mm Hg to atmospheric pressure can be represented by the following equation:

$$\log_{10} P = 0.3389 - \frac{752.5}{T} + 0.011338T$$

where P is the vapor pressure of hydrazine monohydrate in mm Hg and T is the absolute temperature in degrees Kelvin. Vapor pressure values calculated from this equation are compared with the experimental data in Table 1. The maximum deviation between the calculated values and the observed values is about 2% or less, which is probably within the limits of accuracy of the experimental determinations.

Behavior of the Hydrazine Monohydrate in the Vapor Phase. In order to interpret properly the data expressing the increase of pressure with time for the vapor phase oxidation reaction under constant volume conditions, it was necessary to determine if the hydrazine and water molecule comprising hydrazine monohydrate were associated in the vapor phase. Giguire and Rundle[1] have shown that hydrazine molecules do not associate to any appreciable degree in the vapor phase.

The apparatus constructed for the thermal oxidation runs was also used to determine the behavior of pure hydrazine monohydrate in the vapor phase. A measured quantity of hydrazine monohydrate was charged by means of the calibrated pipette directly to the evacuated reactor of known volume. The temperature of the oil bath surrounding the reactor was varied and pressures within the reactor were read at each temperature after thermal equilibrium had been established.

By observing the variation of pressure with temperature, it was possible to determine when all of the hydrazine monohydrate was in the vapor phase. On the basis of the observed

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[1] Giguire and Rundle, *J. Am. Chem. Soc;* 63, 1135 (1941).

pressures and temperatures when all of the hydrazine monohydrate was in the vapor phase, the number of moles of hydrazine and water present were calculated assuming the validity of the perfect gas law, and assuming that the hydrazine monohydrate dissociated completely to pure hydrazine and pure water vapor. The number of moles of vapor in the reactor calculated on the basis of these assumptions was then checked against the number of moles of hydrazine monohydrate originally charged to the reactor. The comparison between the calculated number of moles and the actual number of moles charged to the reactor for the runs made in this series is shown in Tables 2 and 3, page 6.

These results indicate that hydrazine monohydrate dissociates completely into hydrazine vapor and water vapor in the vapor phase at pressures up to at least 500 mm Hg according to the following reaction:

$$N_2H_4 \cdot H_2O(l) \rightarrow N_2H_4(g) + H_2O(g)$$

Table 2. Run B-1

Liquid $N_2H_4 \cdot H_2O$ charged to reactor = 0.415g = 0.00829g moles

Volume of reactor = 888 ml

$n = \frac{PV}{RT} = \frac{(0.01424)(P)}{(t + 273.1)}$ where P = mm Hg and t = °C within reactor.

Reactor Pressure P mm Hg	Reactor Temperature t °C	$n = \frac{0.01424P}{(t + 273.1)}$ moles
436	106.6	.0164
440	108.6	.0164
440	108.8	.0164
443	109.8	.0165
446	112.8	.0165
448	116.0	.0164
450	117.4	.0164
455	118.0	.0166
454.5	119.5	.0165
456	119.6	.0165
474	113.4	.0165
477	133.7	.0167
491	149.2	.0166
491.5	149.4	.0166
492	149.6	.0166
495	151.2	.0166
	Av.	.0165 mols

Moles of gas in reactor calculated from amount of $N_2H_4 \cdot H_2O$ charged assuming 100% dissociation to N_2H_4 gas and H_2O vapor.

n = 0.00829 X 2 = 0.01658 moles

Table 3. Run B-1

Liquid $N_2H_4 \cdot H_2O$ charged to reactor = 0.0716g = 0.00143 g moles

Volume of reactor = 888 ml

$n = \frac{PV}{RT} = \frac{(0.01424)(P)}{(t + 273.1)}$ where P = mm Hg and t = °C within reactor

Reactor Pressure P mm Hg	Reactor Temperature t°C	$n = \frac{0.01424P}{(t + 273.1)}$ moles
68.5	71.2	.00283
70.7	78.8	.00286
73.8	92.8	.00288
74.1	96.4	.00286
74.3	96.8	.00286
	Av.	.00286

Moles of gas in reactor calculated from amount of $N_2H_4 \cdot H_2O$ charged assuming 100% dissociation to N_2H_4 gas and H_2O vapor.

n = .00143 x 2 = .00286 mols

ANALYSIS

The stoichiometric equation for the oxidation of hydrazine monohydrate by oxygen is as follows

$$N_2H_4 \cdot H_2O + O_2 \longrightarrow N_2 + 3H_2O$$

In this investigation the oxidation reaction was carried out in the vapor phase under conditions of constant volume and constant temperature. Since the hydrazine monohydrate molecule dissociates into hydrazine vapor and water vapor in the vapor phase, the overall stoichiometric equation may be represented by

$$N_2H_4 + H_2O \longrightarrow N_2 + 3H_2O$$

The depletion of hydrazine due to this oxidation reaction was measured by observing the pressure rise which occurred in the reactor under conditions of constant volume and constant temperature. The stoichiometric equation for the oxidation of hydrazine by oxygen does not give a true picture of the kinetics of the reaction since there are probably several intermediate reactions which take place. No attempt was made to determine what the intermediate reactions might be since facilities were not available for carrying on a study of this type.

In all of the oxidation runs, the hydrazine monohydrate was charged to the reactor first and then a given quantity of oxygen was charged to the reactor. The reaction began immediately upon the admission of oxygen and there was no indication of an induction period at the beginning of any of the experimental runs.

Insufficient runs were made to complete the study of this reaction because of the termination of the investigation. However, an attempt was made to analyze the results of these runs that were made for the purpose of guiding any further research that might be conducted elsewhere. The results of these runs are included below under the appropriate headings.

Tests of Reaction by Isolation of Reactants. In order to compare reaction rate data, the amount of material which has reacted during a given time interval must be expressed as a function of this time interval. The reduction of experimentally determined reaction rates to an integral reaction rate equation provides a useful basis of comparison. The usual relation for homogeneous reactions conducted at constant temperature and volume is

$$-\frac{dC}{dt} = k_c' C_A^a C_B^b \quad \ldots\ldots\ldots\ldots\ldots\ldots$$

where

C = = concentration, moles per liter

C_A = concentration of component A, moles per liter

C_B = concentration of component B, moles per liter

t = time elapsed in minutes from beginning of reaction

k_c' = specific rate constant

a and b = constants

d = differential operator.

If one reactant, for example, reactant B, is present in large excess during the reaction in comparison to the other reactants, it is depleted only slightly during the reaction and its concentration remains essentially constant. The differential rate equation then assumes the form

$$-\frac{dC}{dt} = k_c C_A^a \qquad \text{where} \quad k_c = k_c' C_B^b$$

If all reactants except one are present in excess, the effect of the concentration of the selected reactant upon the rate of reaction can be determined. If the reaction is a simple homogeneous one, the order of the reaction with respect to the selected reactant can be determined by this isolation technique.

A series of runs was made wherein hydrazine monohydrate was isolated by charging a large excess of oxygen to the reactor. These runs were made at a temperature of about 99°C and the quantity of hydrazine monohydrate charged to the reactor was varied from 0.000392 moles to 0.00139 moles. The stoichiometric quantity of oxygen required in each of the runs is numerically equal to the quantity of hydrazine monohydrate. In order that an excess of oxygen be present, the moles of oxygen charged to the reactor were varied from 0.00678 moles to 0.00935 moles. The reaction was assumed to be first order with respect to hydrazine, and the reaction rate constant was calculated from the first order integral rate equation.

$$k_c = \frac{1}{t} \ln \left(\frac{N_0}{N_0 - X} \right)$$

where

N_0 = moles of hydrazine present in the reactor at the beginning of the reaction

X = moles of hydrazine reacted at time t

k_c = specific rate constant, min.^{-1}

The results of this series of runs are shown in Tables 4,5,6, and 7 with the calculated values of k_c at various time intervals. The data are plotted in Fig. 4. It may be seen from

Table 4. Test of reaction for first order with respect to hydrazine. Run E-1. Temp. = 99.2°C.

Reactor Volume = 888 ml
Moles hydrazine monohydrate charged to reactor = 0.000392
Moles oxygen charged to reactor = 0.00935

Time elapsed, minutes	Reactor Pressure, mm Hg	$\frac{N_0}{N_0-X}$	k_c min.$^{-1}$
0	264.1	1.0	
1:00	266.0	1.27	0.240
2:30	267.8	1.64	0.215
3:00	269.0	2.02	0.234
4:00	270.0	2.51	0.230
5.00	270.7	3.04	0.223
6:00	271.2	3.56	0.212
7:00	271.8	4.51	0.215
8:00	272.5	6.54	0.235
9:00	273.0	9.56	0.250
10:00	273.3	13.06	0.256

Table 5. Test of reaction for first order with respect to hydrazine. Run E-2. Temp. = 99.2°C

Reactor volume = 888 ml
Moles hydrazine monohydrate charged to reactor = 0.000688
Moles oxygen charged to reactor = 0.00894

Time elapsed, minutes	Reactor Pressure, mm Hg	$\frac{N_0}{N_0-X}$	k_c min.$^{-1}$
0	260.0	1.00	
1:00	261.4	1.08	0.080
2:00	262.5	1.16	0.074
3:00	263.7	1.26	0.076
4:00	265.0	1.38	0.081
5:00	266.1	1.51	0.083
6:00	267.3	1.68	0.087
7:00	268.4	1.87	0.089
8:00	269.4	2.08	0.092
9:00	270.4	2.36	0.096
10:00	271.2	2.66	0.098
11:00	272.0	2.98	0.099
12:00	272.7	3.36	0.101
13:00	273.2	3.70	0.108
14:00	274.1	4.55	0.110
15:00	274.6	5.25	0.113
16:00	275.1	6.09	0.116

Table 6. Test of reaction for first order with respect to hydrazine.
Run E-3. Temp. = 99.8°C

Reactor volume = 888 ml
Moles hydrazine monohydrate charged to reactor = 0.000935
Moles oxygen charged to reactor = 0.00766

Time elapsed, minutes	Reactor Pressure mm Hg	$\frac{N_0}{N_0-X}$	k_c min.$^{-1}$
0	250.0	1.00	
1:30	252.5	1.11	0.070
2:00	253.2	1.15	0.070
3:00	254.4	1.22	0.066
4:00	255.7	1.30	0.066
5:00	256.9	1.39	0.066
6:00	258.1	1.49	0.067
7:00	259.2	1.60	0.067
8:00	260.2	1.71	0.067
9:00	261.2	1.84	0.068
10:00	262.2	1.99	0.069
11:00	263.1	2.14	0.069
12:00	264.1	2.36	0.072
13:00	265.0	2.57	0.073
14:00	265.9	2.84	0.075
16:00	267.0	3.26	0.074
19:00	269.0	4.45	0.079
20:00	269.5	4.87	0.079
24:00	271.3	7.6	0.084

Table 7. Test of reaction for first order with respect to hydrazine.
Run E-4. Temp. = 99.8°C.

Reactor volume = 888 ml
Moles hydrazine monohydrate charged to reactor = 0.00139
Moles oxygen charged to reactor = 0.00678

Time elapsed minutes	Reactor Pressure mm Hg	$\frac{N_0}{N_0-X}$	k_c min.$^{-1}$
0	250.8	1.00	
1:00	252.8	1.06	0.058
2:00	254.4	1.11	0.052
3:00	256.0	1.17	0.052
4:00	257.6	1.23	0.052
5:00	259.1	1.30	0.053
6:00	260.4	1.36	0.051
7:00	261.8	1.41	0.049
8:00	263.2	1.51	0.052
9:00	264.3	1.60	0.052
17:00	273.2	2.67	0.058
18:00	274.0	2.78	0.057
21:00	276.2	3.48	0.059
24:00	278.3	4.10	0.049
28:00	280.6	5.56	0.061

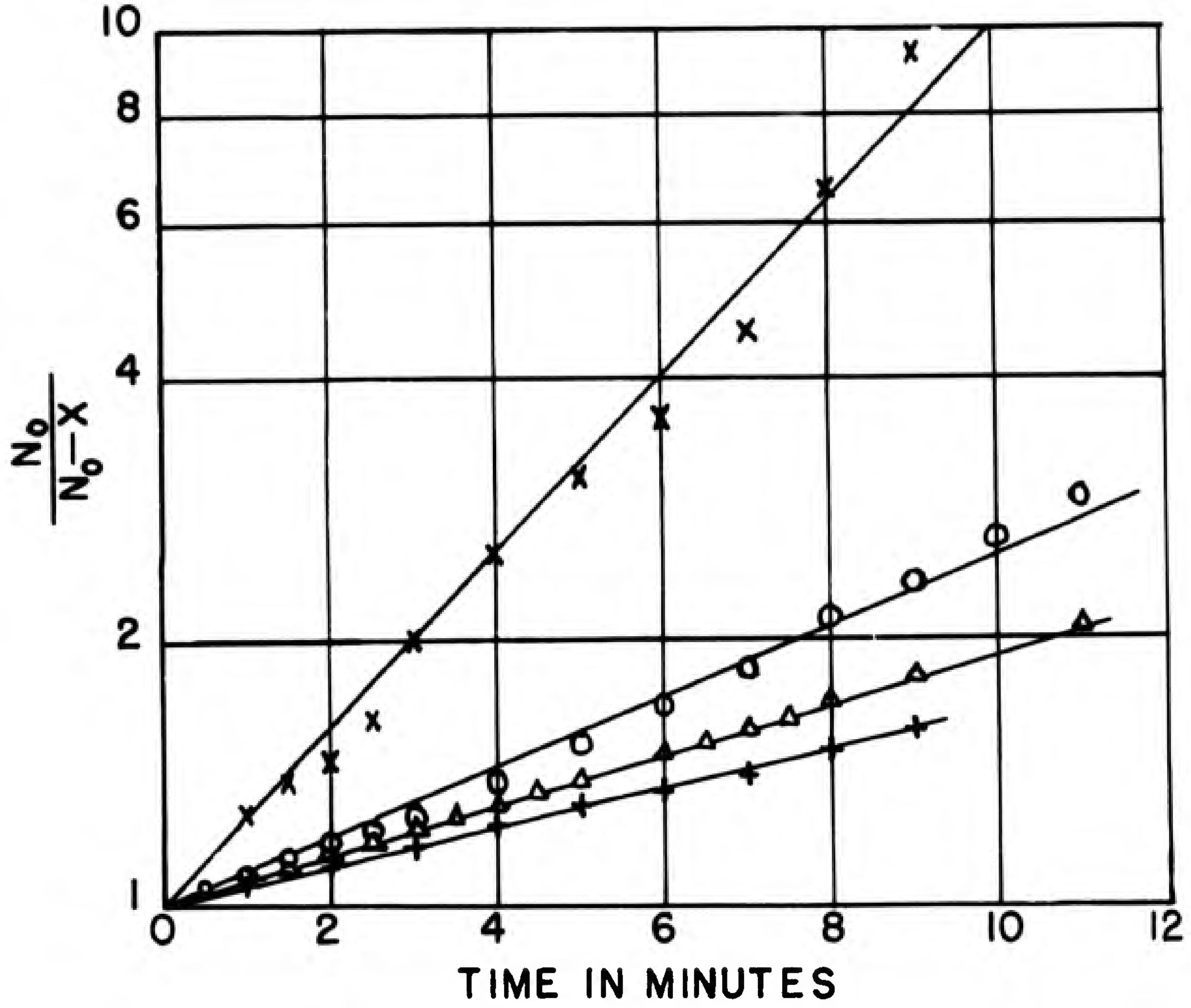

Fig. 4. Test of reaction for first order with respect to hydrazine.
X - Run E-1
O - Run E-2
Δ - Run E-3
+ - Run E-4

Fig. 4 and the values of k_c in Tables 4 to 7, that the individual runs may be represented approximately by a first order equation.

However, it is apparent that as the amount of hydrazine monohydrate charged was increased, the specific rate constant decreased in value and that there was a tendency for the values to increase during the reaction. This would seem to indicate that something other than a simple first order reaction actually occurred.

One run was made at 100°C wherein oxygen was isolated (hydrazine monohydrate charged in excess). The reaction was assumed to be first order with respect to oxygen and the reaction rate constant was calculated from the first order integral rate equation. The results of this run are shown in Table 8 with the calculated values of k_c. The data are plotted in Fig. 5. The data indicate that the reaction may be represented very well as first order with respect to oxygen.

Table 8. Test of reaction for first order with respect to oxygen.
Run F-1. Temp. = 100°C.

Reactor volume = 888 ml
Moles oxygen charged to reactor = 0.000794
Moles of hydrazine monohydrate charged to reactor = 0.00399

Time elapsed minutes	Reactor Pressure mm Hg	$\frac{N_0}{N_0-X_0}$	k_c min^{-1}
0	230.0	1.0	--
2	231.7	1.09	0.028
3	232.3	1.12	0.028
4	232.8	1.15	0.027
5	233.3	1.19	0.029
6	233.9	1.23	0.030
7	234.3	1.26	0.029
8	234.9	1.31	0.030
10	235.9	1.40	0.031
12	236.8	1.49	0.031
15	237.9	1.61	0.030
16	238.2	1.65	0.030
18	239.0	1.76	0.030
20	239.7	1.87	0.029
26	241.3	2.19	0.029
30	242.3	2.45	0.028

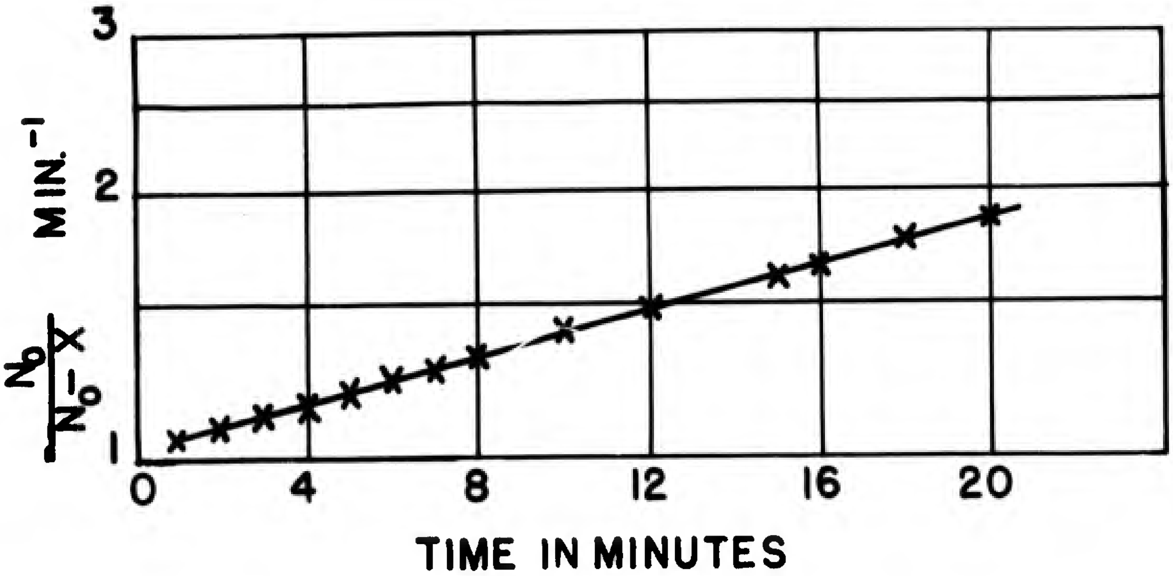

Fig. 5. Test of reaction for first order with respect to oxygen.

Test of Reaction for Second Order. On the basis of the information gained about the approximate order of the reaction by the isolation technique, an effort was made to represent the reaction as one kinetically of the second order. The second order specific rate constant k_c' was calculated by the following equation:

$$k_c' = \left(\frac{V}{N_0 t}\right)\left(\frac{X}{N_0 - X}\right)$$

k_c' = second order specific rate constant, liters/(mole)(min.)

V = volume of reactor in liters = 0.888 liters

N_0 = mols hydrazine monohydrate charged to reactor

N_0 = mols oxygen charged to reactor

X = mols of hydrazine and of oxygen which have reacted at time t

t = time, minutes

The above equation was used because essentially equal amounts of hydrazine and oxygen were charged to the reactor in all the runs made in this series.

Examination of the values of k_c' given in Tables 9 to 16 shows considerable disagreement between different runs. Runs C-7, C-8, and C-9 which were conducted under essentially the same conditions on consecutive days are in good agreement with one another. However, they are in considerable disagreement with runs C-2 and C-6 which were conducted about a month earlier in the same apparatus. No satisfactory explanation can be given for this discrepancy except to suggest that some change in condition of the surface of the reactor might be responsible. It may be noticed that the values of k_c' calculated for runs C-11, C-12, and C-13 are in fair agreement with one another but are not in agreement with the values for runs C-7, C-8, and C-9. It may be also noticed that a larger quantity of hydrazine monohydrate and oxygen were charged in runs C-7, C-8, and C-9 than in runs C-11, C-12, and C-13.

In every case the value of k_c' increases slowly as the reaction proceeds. Since the increase in k_c' can be expressed as a function of the degree of completion of the reaction, it is natural to assume either that the reaction is not second order with respect to both hydrazine and oxygen (*i.e.*, first order with respect to each) or that some other component which is present has an effect upon the rate of reaction.

In order to determine the effect of the products of the reaction, nitrogen and water vapor, upon the rate, runs were made with different amounts of each charged to the reactor. The results of the runs in which water vapor was charged in excess are shown in Tables 17, 18, and 19 and are plotted in Fig. 6. If the reaction is one of second order, a plot of $(X/N_0\text{-}X)$ versus time should be linear. The data do not give a linear relationship, however, the curvature of the lines is small and the rates of the reaction may be compared on the

Table 9. Test of reaction for second order.
Run C-2. Temp. = 102.4°C

Reactor volume = 888 ml
Moles of hydrazine monohydrate charged to reactor = 0.00386
Moles of oxygen charged to reactor = 0.00386

Time elapsed minutes	Reactor Pressure mm Hg	$\frac{X}{N_0-X}$	k_c' liter/(mol)(min.)
0	305.0	0	
8:00	330.0	0.326	8.58
12:00	337.8	0.474	8.58
14:00	342.0	0.569	9.25
18:00	348.0	0.746	9.34
26:00	357.2	1.05	9.15
34:00	364.5	1.41	9.50
42:00	369.6	1.76	9.60
50:00	374.1	2.14	9.40
60:00	378.0	2.54	9.70
74:00	382.9	3.30	10.3
80:00	384.4	3.60	10.4

Table 10. Test of reaction for second order.
Run C-6. Temp. = 97.4°C.

Reactor volume = 888 ml
Moles of hydrazine monohydrate charged to reactor = 0.00402
Moles of oxygen charged to reactor = 0.00402

Time elapsed minutes	Reactor Pressure mm Hg	$\frac{X}{N_0-X}$	k_c' liter/(mol)(min.)
0	315.0	0	
2:00	326.4	0.120	13.0
4:00	335.8	0.248	13.4
6:00	343.6	0.372	13.5
8:00	350.3	0.505	13.7
10:00	356.2	0.648	13.9
12:00	361.5	0.795	14.3
16:00	370.0	1.10	14.7
20:00	377.1	1.45	15.2
30:00	389.2	2.32	16.0
36:00	394.0	3.04	18.6
42:00	398.0	3.77	19.8

Table 11. Test of reaction for second order.
Run C-7. Temp. = 97.3°C

Reactor volume = 888 ml
Moles hydrazine monohydrate charged to reactor = 0.00399
Moles of oxygen charged to reactor = 0.00399

Time elapsed minutes	Reactor Pressure mm Hg	$\frac{X}{N_0-X}$	k_c' liters/(mol)(min.)
0	312.0	0	--
2:00	321.0	0.118	10.2
3:00	325.1	0.167	10.6
4:00	329.0	0.220	11.0
5:00	332.4	0.271	11.1
6:00	336.0	0.325	11.3
7:00	339.2	0.386	11.6
8:00	342.4	0.445	11.9
9:00	345.2	0.489	11.6
11:00	350.6	0.622	12.3
12:00	353.0	0.683	12.4
14:00	357.6	0.821	12.8
16:00	361.7	0.956	13.1
18:00	365.2	1.09	13.3
20:00	368.8	1.26	13.9
24:00	374.5	1.51	14.0
28:00	379.2	1.90	15.0
32:00	383.0	2.22	15.4

Table 12. Test of reaction for second order.
Run C-8. Temp. = 97.3°C.

Reactor volume = 888 ml
Moles of hydrazine monohydrate charged to reactor = 0.00407
Moles of oxygen charged to reactor = 0.00407

Time elapsed minutes	Reactor pressure mm Hg	$\frac{X}{N_0-X}$	k_c' liters/(mol)(min.)
0	318.0	0	--
2:00	327.1	0.091	9.1
3:00	332.1	0.150	11.0
4:00	336.0	0.204	11.3
5:00	339.9	0.260	11.5
6:00	343.5	0.313	11.6
7:00	347.0	0.375	11.8
9:00	353.0	0.491	12.1
10:00	356.0	0.554	12.3
12:00	361.2	0.689	12.7
14:00	366.0	0.825	13.1
18:00	374.0	1.12	13.8
22:00	380.0	1.41	14.1
26:00	385.3	1.73	14.7
30:00	389.6	2.04	15.0

Table 13. Test of reaction for second order.
Run C-9. Temp. = 97.4°C

Reactor volume = 888 ml
Moles of hydrazine monohydrate charged to reactor = 0.00406
Moles of oxygen charged to reactor = 0.00406

Time elapsed minutes	Reactor Pressure mm Hg	$\frac{X}{N_0-X}$	k'_c liters/(mol)(min.)
0	318.0	0	--
2:00	328.4	0.106	10.7
3:00	332.8	0.160	11.2
4:00	337.0	0.216	11.6
5:00	341.0	0.276	11.9
6:00	344.5	0.331	12.0
8:00	351.0	0.450	12.3
10:00	357.0	0.580	12.7
12:00	362.0	0.706	12.9
14:00	367.0	0.855	13.4
18:00	374.9	1.148	14.0
22:00	381.0	1.460	14.6
28:00	388.5	1.988	15.6

Table 14. Test of reaction for second order.
Run C-11. Temp. = 100.4°C.

Reactor volume = 888 ml
Moles of hydrazine monohydrate charged to reactor = 0.00340
Moles of oxygen charged to reactor = 0.00340

Time elapsed minutes	Reactor Pressure mm Hg	$\frac{X}{N_0-X}$	k'_c liters/(mol)(min.)
0	266.0	0	--
2:00	271.4	0.0625	8.2
3:00	274.0	0.100	8.7
4:00	276.3	0.130	8.5
5:00	279.0	0.173	9.0
6:00	281.0	0.201	8.8
7:00	283.0	0.236	8.8
8:00	285.0	0.268	8.8
9:00	287.2	0.312	9.1
10:00	289.1	0.349	9.2
12:00	292.8	0.428	9.3
14:00	296.0	0.505	9.4
16:00	299.8	0.611	9.9
18:00	301.8	0.674	9.8
20:00	304.3	0.752	9.8
22:00	307.0	0.858	10.2
24:00	309.0	0.931	10.1
28:00	312.8	1.11	10.4
32:00	316.2	1.30	10.7
36:00	320.0	1.54	11.2
40:00	321.5	1.66	10.8
60:00	330.5	2.63	11.5

Table 15. Test of reaction for second order.
Run C-12. Temp. = 100.2°C

Reactor volume = 888 ml
Moles of hydrazine monohydrate charged to reactor = 0.00352
Moles of oxygen charged to reactor = 0.00352

Time elapsed, minutes	Reactor Pressure mm Hg	$\frac{X}{N_0 - X}$	k'_c liters/(mol)(min.)
0	278	0	--
2:00	284.8	0.083	9.0
3:00	287.6	0.121	9.2
4:00	290.2	0.154	9.0
6:00	295.1	0.231	9.2
8:00	299.6	0.308	9.4
10:00	303.8	0.391	9.6
12:00	306.8	0.460	9.7
15:00	312.0	0.585	9.7
18:00	318.0	0.769	10.6
24:00	326.0	1.09	11.5
30:00	332.0	1.43	12.0
32:00	334.3	1.59	12.5
36:00	337.3	1.82	12.8
40:00	340.2	2.09	13.1
44:00	343.0	2.42	13.9
48:00	345.0	2.68	14.1
60:00	349.8	3.58	15.0

Table 16. Test of reaction for second order.
Run C-13. Temp. = 99.6°C

Reactor volume = 888 ml
Moles of hydrazine monohydrate charged to reactor = 0.00348
Moles of oxygen charged to reactor = 0.00348

Time elapsed minutes	Reactor Pressure mm Hg	$\frac{X}{N_0-X}$	k_c' liters/ (mol) (min.)
0	272.5	0.0	--
2:00	278.4	0.064	8.2
3:00	281.2	0.101	8.6
4:00	283.9	0.137	8.8
5:00	286.4	0.176	9.0
6:00	288.8	0.208	8.9
8:00	293.1	0.284	9.1
10:00	297.3	0.364	9.3
12:00	301.3	0.450	9.6
14:00	305.0	0.540	9.9
16:00	308.2	0.635	10.1
18:00	311.1	0.722	10.2
24:00	319.0	1.02	10.8
28:00	323.2	1.23	11.2
32:00	327.0	1.47	11.6
37:00	331.0	1.76	12.2
40:00	331.1	1.95	12.4
44:00	335.6	2.20	12.8
48:00	337.8	2.48	13.1
52:00	339.8	2.76	13.5
60:00	343.0	3.35	14.3

Table 17. Effect of water vapor upon rate of reaction.
Run D-1. Temp. = 99.6°C
Reactor Volume = 888 ml.

Moles of hydrazine monohydrate charged to reactor = 0.00353
Moles of oxygen charged to reactor = 0.00353
Moles of water vapor initially present in reactor = 0.01003

Time elapsed minutes	Reactor Pressure mm Hg	$\frac{X}{N_0-X}$	k_c' liters/(mol)(min)
0	446.5	0	
4:00	471.1	0.363	25.7
5:00	474.5	0.435	24.7
7:00	481.3	0.605	24.5
8:00	483.9	0.680	24.1
9:00	486.5	0.765	24.1
10:00	489.0	0.849	24.1
12:00	493.0	1.008	23.9
15:00	498.5	1.278	24.2
16:00	500.0	1.370	24.3
18:00	502.7	1.540	24.2
20:00	505.3	1.74	24.6

Table 18. Effect of water vapor upon rate of reaction.
Run D-2. Temp. = 99.6°C
Reactor Volume = 888 ml.

Moles of hydrazine monohydrate charged to reactor = 0.00350
Moles of oxygen charged to reactor = 0.00350
Moles of water vapor initially present in reactor = 0.00679

Time elapsed minutes	Reactor pressure mm Hg	$\frac{X}{N_0-X}$	k_c' liters/(mol)(min)
0	360.0	0	
3:00	371.8	0.1514	14.4
4:00	375.0	0.1987	14.2
5:00	378.1	0.250	14.3
6:00	381.0	0.298	14.2
7:00	383.6	0.352	14.4
8:00	386.0	0.400	14.3
9:00	388.4	0.453	14.4
10:00	390.6	0.509	14.5
11:00	393.0	0.569	14.8
12:00	394.8	0.620	14.8
14:00	398.8	0.741	15.1
16:00	402.1	0.862	15.4
18:00	405.1	0.977	15.5
20:00	408.0	1.108	15.8

Table 19. Effect of water vapor upon rate of reaction.
Run D-3. Temp. = 99.6°C.
Reactor Volume = 888 ml.

Moles of hydrazine monohydrate charged to reactor = 0.00348
Moles of oxygen charged to reactor = 0.00348
Moles of water vapor initially present in reactor = 0.00844

Time elapsed minutes	Reactor pressure mm Hg	$\frac{X}{N_0 - X}$	k'_c liters/(mol)(min)
0	404.0	0	
2:00	415.0	0.137	19.6
3:00	418.5	0.192	18.4
4:00	422.5	0.256	18.4
5:00	425.8	0.318	18.3
6:00	438.9	0.375	18.0
7:00	441.9	0.445	18.3
8:00	444.6	0.506	18.2
9:00	447.1	0.575	18.4
10:00	449.5	0.642	18.5
11:00	451.7	0.705	18.4
12:00	453.8	0.775	18.5
13:00	455.8	0.851	18.8
14:00	457.7	0.924	18.9
17:00	462.6	1.149	19.4
18:00	463.8	1.202	19.2
20:00	466.8	1.385	19.9
22:00	468.8	1.520	19.8

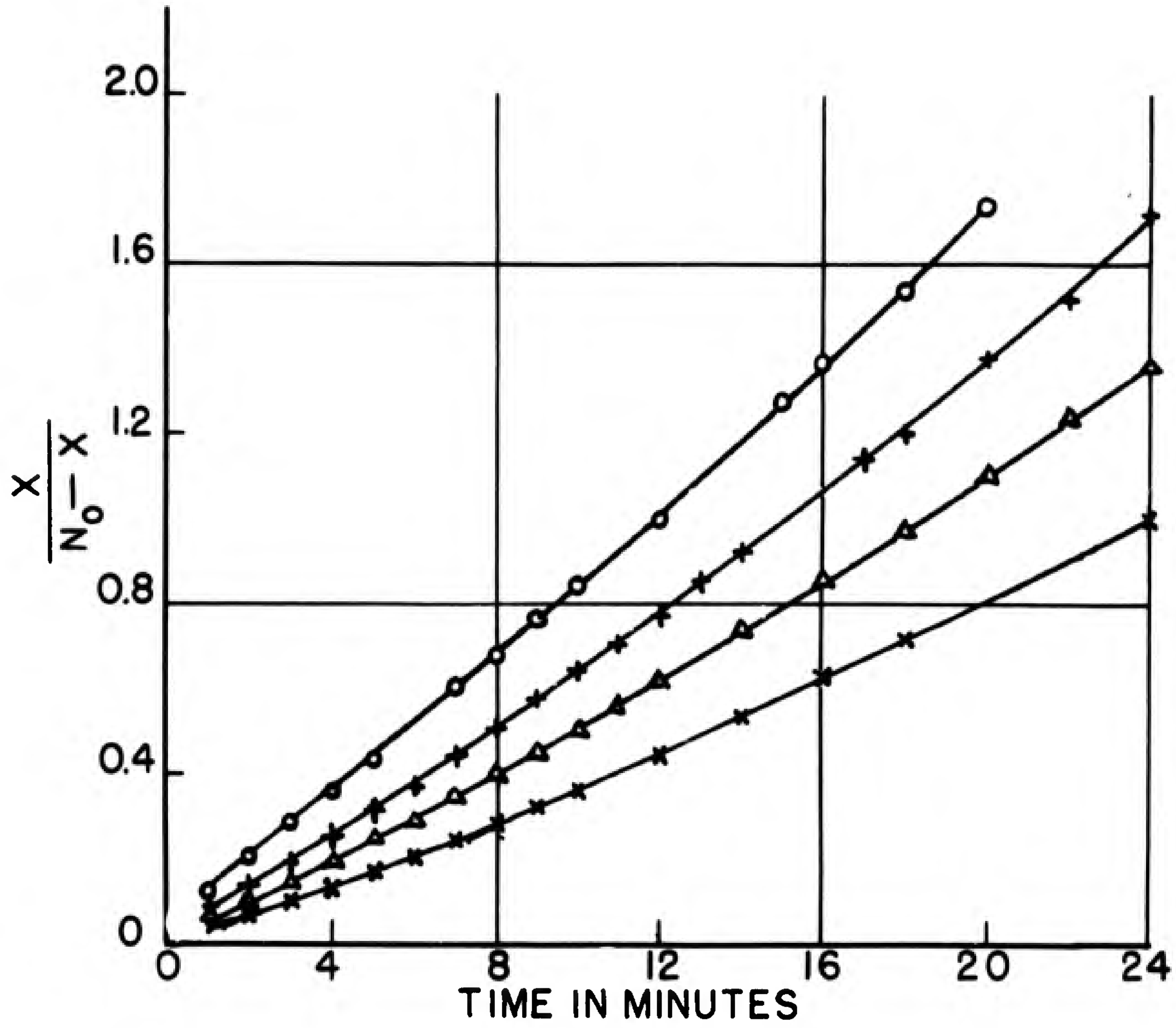

Fig. 6. Effect of water vapor upon rate of reaction.

O-Run D-1 N_{wo} = 0.01003 mols

Δ-Run D-2 N_{wo} = .00679

+-Run D-3 N_{wo} = .00844

X-Run C-13 N_{wo} = .00348

basis of a second order reaction. The term (X/N_0-X) is a measure of the degree of completion of the reaction. Inspection of Fig. 6 shows that an increase in the number of moles of water, N_{wo}, initially present in the reactor causes an increase in the rate of reaction; therefore, it may be concluded that water vapor has a catalytic effect upon the reaction.

The results of the runs in which nitrogen was charged in excess to the reactor are shown in Tables 20, 21, and 22 and are plotted in Fig. 7. Although these data show a slight difference in the rate of reaction, the effect of the number of moles of nitrogen, N_{no}, initially present in the reactor is perhaps negligible. The slight differences in reaction rate indicated in Fig. 7 could have been caused by other effects such as the condition of the reactor surface or differences in the quantity of hydrazine monohydrate or oxygen initially charged to the reactor. In any event the effect of nitrogen upon the reaction is much less than the effect of water vapor.

Dependence of the Reaction Rate upon Water Vapor Concentration. As pointed out in the previous section, increasing the water vapor concentration increased the rate of the reaction. Since water is a product of the reaction, and is also present initially in a concentration at least equal to that of the hydrazine present, it would be expected that the specific rate constant, k_c', calculated for a reaction kinetically of the second order with respect to hydrazine and oxygen, would increase in value as the reaction proceeds. Such an effect was observed in every case in the preceding series of experiments. It should be possible to find an equation which would take into account the effect of the amount of water present. From the stoichiometric equation for the oxidation of hydrazine monohydrate by oxygen

$$N_2H_4 + H_2O + O_2 \longrightarrow N_2 + 3H_2O$$

a differential rate equation of the form

$$\frac{dx}{dt} = k_c'' \frac{(N_0-X)^2 (N_{wo} + 2x)^n}{V^{2+n}}$$

may be written which expresses the rate of reaction as being proportional to the *nth* power of the amount of water vapor, $N_{wo} + 2X$, present at any time t. Such a differential equation might be called a rate equation for an *autocatalytic reaction of the 2 + n order.*

If the differential rate equations for the second order and the 2+n order autocatalytic reactions are compared,

$$\frac{dx}{dt} = k_c' \frac{(N_0-X)^2}{V^2}$$

$$\frac{dx}{dt} = k_c'' \frac{(N_0-X)^2 (N_{wo} + 2x)^n}{V^{2+n}}$$

Table 20. Effect of nitrogen upon rate of reaction
Run G-1. Temp. = 100.0 C.
Reactor volume = 888 ml.

Moles of hydrazine monohydrate charged to reactor = 0.00343
Moles of oxygen charged to reactor = 0.00343
Moles of nitrogen charged to reactor = 0.00344

Time elapsed minutes	Reactor pressure mm Hg	$\frac{X}{N_0 \; X}$	k_c' liters/(mol)(min)
0	360.5	0	
1:00	364.0	0.0395	11.5
2:00	367.1	0.079	11.4
3:00	369.7	0.114	11.1
4:00	372,6	0.155	11.3
5:00	375.4	0.195	11.4
6:00	377.8	0.234	11.4
8:00	382.5	0.324	11.8
10:00	386.5	0.406	11.9
12:00	390.6	0.497	12.1
14:00	394.5	0.610	12.7
16:00	397.6	0.698	12.7
20:00	403.3	0.905	13.2

Table 21. Effect of nitrogen upon rate of reaction.
Run G-2. Temp. = 100.0°C
Reactor volume = 888 ml

Moles of hydrazine monohydrate charged to reactor = 0.00360
Moles of oxygen charged to reactor = 0.00360
Moles of nitrogen charged to reactor = 0.00522

Time elapsed minutes	Reactor Pressure mm Hg	$\frac{X}{N_0 - X}$	k_c' liters/(mol)(min)
0	419.0	0	
1:00	423.2	0.0465	13.3
2:00	426.8	0.0876	12.2
3:00	429.5	0.125	11.6
4:00	432.8	0.169	11.8
6:00	438.6	0.259	12.0
8:00	444.0	0.358	12.4
9:00	446.1	0.400	12.3
12:00	452.4	0.545	12.6
16:00	460.0	0.765	13.3
20:00	466.0	0.989	13.7
28:00	475.0	1.518	15.1
30:00	476.5	1.552	14.4

Table 22. Effect of nitrogen upon rate of reaction.
Run G-3. Temp. = 100.0°C
Reactor Volume = 888 ml

Moles of hydrazine monohydrate charged to reactor = 0.00353
Moles of oxygen charged to reactor = 0.00353
Moles of nitrogen charged to reactor = 0.00642

Time elapsed minutes	Reactor Pressure mm Hg	$\frac{X}{N_0 - X}$	k'_c liters/(mol)(min)
0	445.8	0	
1:00	449.0	0.0352	10.0
2:00	452.0	0.0696	9.9
3:00	455.0	0.110	10.4
4:00	458.0	0.150	10.6
6:00	463.8	0.239	11.3
8:00	468.8	0.327	11.9
10:00	473.1	0.418	12.2
12:00	477.5	0.522	12.7
16:00	485.0	0.730	13.3
20:00	491.0	0.950	13.8
25:00	497.0	1.235	14.0
30:00	502.2	1.555	14.7
36:00	507.2	1.967	15.5

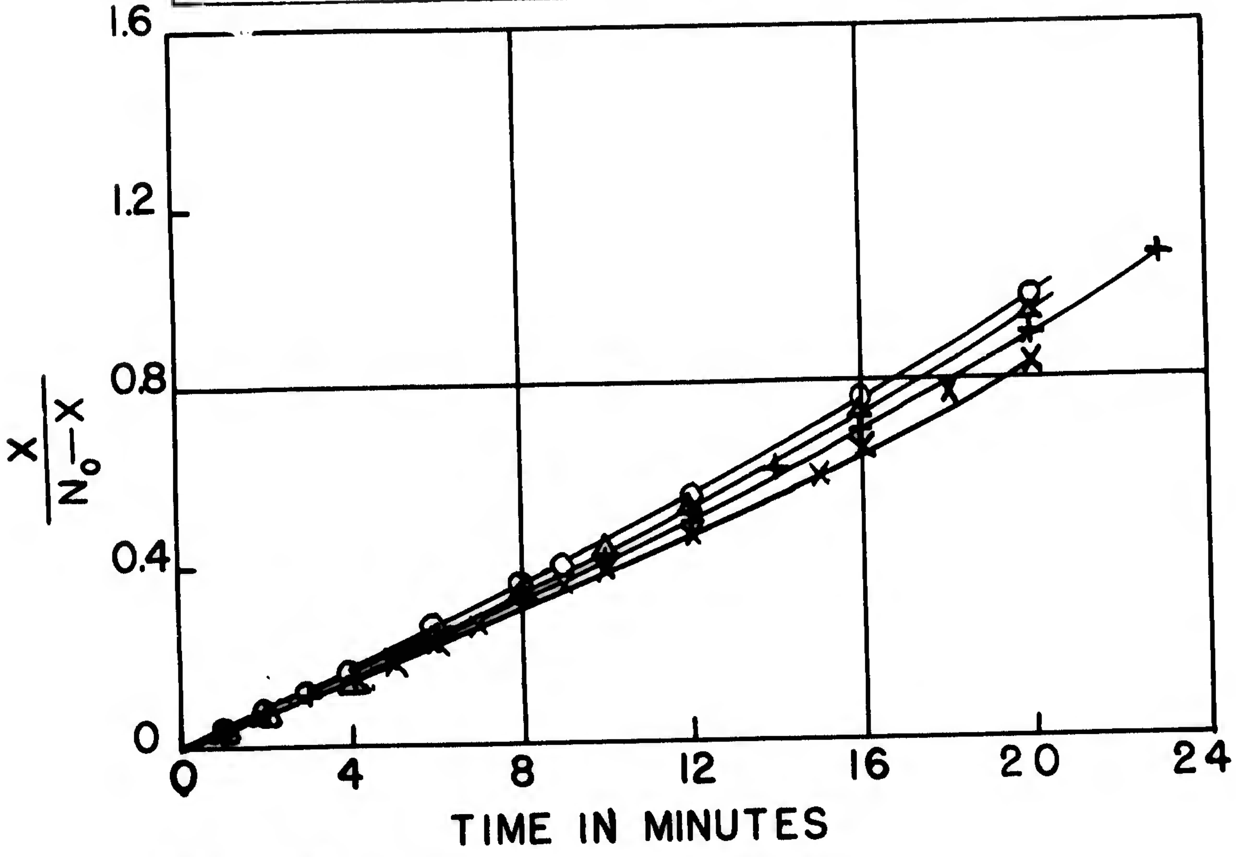

Fig. 7. Effect of nitrogen upon rate of reaction.
+-Run G-1 N_{no} = .00344 mols
O-Run G-2 N_{no} = .00522
Δ-Run G-3 N_{no} = .00642
X-Run C-12 N_{no} = 0

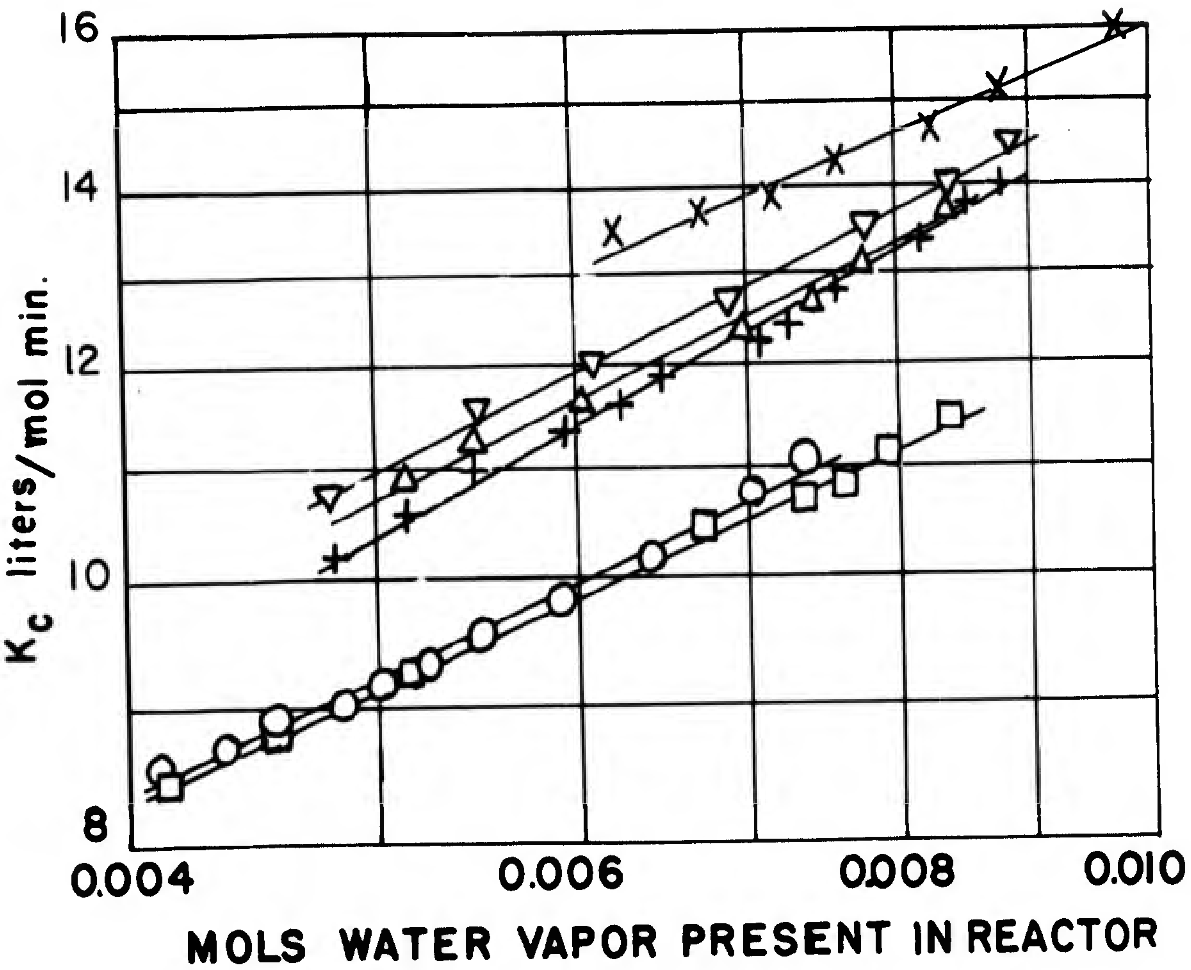

Fig. 8. Effect of water vapor upon k_c' calculated for a second order reaction.

X-Run C-6
+-Run C-7
Δ-Run C-8
∇-Run C-9
□-Run C-11
O-Run C-13

it is evident that k_c', the specific rate constant for the second order reaction is equal to $k_c''(N_{wo} + 2n)^n/V^n$ where k_c'' is the specific rate constant for the $(2+n)$ order reaction. It follows that the following relation is also true:

$$\log k_c = \log \frac{k_c''}{V^n} + n \log (N_{wo} + 2X)$$

The value of n may be found by plotting $\log k_c'$ versus $\log (N_{wo}+2X)$, and measuring the slopes of the curves. If the reaction can be represented by the proposed autocatalytic equation, the value of k_c'' will be constant as will the slopes of the curves.

To check the possibility that the reaction for the oxidation of hydrazine monohydrate by oxygen might be represented by such an equation, a plot of $\log k_c$ versus $\log (N_{wo}+2X)$ was made for a number of runs. The result of this plot is shown in Fig. 8. As may be seen, straight lines are obtained. The slopes of these lines vary from about 0.4 to 0.5 but are in satisfactory agreement with one another. Three runs gave curved lines which might indicate that some other effect besides that of catalysis by water was dominant, or that the measurements were not of sufficient accuracy to give consistent results by this method. The data for these three runs are not plotted in Fig. 8. Even though the rate might be proportional in some manner to the amount of water present, the form of this relationship might be far more complicated than the simple power function of the concentration. Nevertheless, since the plots did give straight lines, the relationship may be expressed in the conventional power form.

If the average value of the slope of the lines in Fig. 8 is taken as 0.5, the differential rate equation may be written as:

$$\frac{dx}{dt} = k_c'' \frac{(N_O - X)^2 (N_{wo} + 2X)^{\frac{1}{2}}}{V^{2\frac{1}{2}}}$$

which may be integrated to give the integral rate equation for an autocatalytic reaction of the 2.5 kinetic order. The specific rate constant, k_c'', may be calculated from the integral equation in the following form:

$$k_c'' = \frac{V^{\frac{3}{2}}}{t} \left[\frac{\sqrt{N_{wo} + 2X}}{(2N_O + N_{wo})(N_O - X)} + \frac{1}{(2N_O + N_{wo})^{\frac{3}{2}}} \ln \left(\frac{\sqrt{2N_O + N_{wo}} + \sqrt{N_{wo} + 2X}}{\sqrt{2N_O + N_{wo}} - \sqrt{N_{wo} + 2X}} \right) \right] + C$$

Values of k_c'' were calculated for several runs using the above equations, and are given in Tables 23 through 29.

The values of k_c'' given in Tables 23 through 29 indicate that the individual runs on the oxidation of hydrazine monohydrate by oxygen may be represented very well by a rate equation for an autocatalytic reaction of the 2.5 order. To clarify what is meant by an autocatalytic reaction of the 2.5 order for this case, the following differential rate equation is written for the rate of disappearance by reaction, dx/dt, of the reactants, namely, hydrazine and oxygen.

$$\frac{dx}{dt} = k_c'' (N_2H_4)^1 (O_2)^1 (H_2O)^{0.5}$$

The quantities in parentheses represent concentrations of the respective constituents. The above differential equation states that the rate of reaction is proportional to the first power of the hydrazine, to the first power of the oxygen, and to the 0.5 power of the water concentrations. The integral reaction rate equation obtained from this differential form is the one that most satisfactorily relates the degree of completion of the reaction to the time that the system has reacted.

Table 23. Calculation of k_c'' for a 2.5 order autocatalytic reaction. Run C-2. Temp. = 102.4°C

N_O = 0.00386 mols of hydrazine and mols of oxygen charged initially to the reactor

N_{wo} = 0.00386 mols of water charged initially to reactor

Time elapsed minutes	Reactor Pressure mm Hg	X mols	k_c'' liters$^{3/2}$/mol$^{3/2}$min
0	305.0	0.	---
8:00	330.0	0.00095	113
10:00	334.0	0.00110	109
12:00	337.8	0.00124	107
18:00	348.0	0.00165	113
26:00	357.2	0.00198	106
34:00	364.5	0.00226	108
50:00	374.1	0.00263	106

Table 24. Calculation of k_c'' for a 2.5 order autocatalytic reaction. Run C-6. Temp. = 97.4°C

N_O = 0.00402 mols of hydrazine and mols of oxygen charged initially to the reactor

N_{wo} = 0.00402 mols of water charged initially to reactor

Time elapsed minutes	Reactor Pressure mm Hg	X mols	k_c'' liters$^{3/2}$/mol$^{3/2}$ min
0	315.0	0	---
2:00	326.4	0.00043	183
6:00	343.6	0.00109	177
8:00	350.3	0.00135	179
10:00	356.2	0.00158	176
12:00	361.5	0.00178	177
16:00	370.0	0.00211	178
20:00	377.1	0.00238	181
30:00	389.2	0.00284	189
36:00	394.0	0.00303	194

Table 25. Calculation of k_c'' for a 2.5 order autocatalytic reaction.
Run C-7. Temp. = 97.3°C.

N_o = 0.00399 mols of hydrazine and mols of oxygen charged initially to the reactor

N_{wo} = 0.00399 mols of water charged initially to reactor.

Time elapsed minutes	Reactor Pressure mm Hg	X mols	k_c'' liters$^{3/2}$/mol$^{3/2}$min
0	312.0	0	---
3:00	325.1	0.00057	171
4:00	329.0	0.00072	167
5:00	332.4	0.00085	164
6:00	336.0	0.00098	162
8:00	342.4	0.00123	162
11:00	350.6	0.00153	166
12:00	353.0	0.00162	159
14:00	357.6	0.00180	162
16:00	361.7	0.00195	160
20:00	368.8	0.00222	162
24:00	374.5	0.00240	159

Table 26. Calculation of k_c'' for a 2.5 order autocatalytic reaction.
Run C-8. Temp. = 97.3°C

N_o = 0.00407 mols of hydrazine and mols of oxygen charged initially to the reactor

N_{wo} = 0.00407 mols of water charged initially to reactor.

Time elapsed minutes	Reactor pressure mm Hg	X mols	k_c'' liters$^{3/2}$/mol$^{3/2}$min
0	318.0	0	---
3:00	332.1	0.00053	152
4:00	336.0	0.00069	152
6:00	343.5	0.00097	151
10:00	356.0	0.00145	152
12:00	361.2	0.00166	152
14:00	366.0	0.00184	154
18:00	374.0	0.00215	156
22:00	380.0	0.00238	156
26:00	385.3	0.00258	160
30:00	389.6	0.00275	160

Table 27. Calculation of k_c'' for a 2.5 order autocatalytic reaction. Run C-9. Temp. = 97.4°C

N_0 = 0.00406 mols of hydrazine and mols of oxygen charged initially to the reactor

N_{wo} = 0.00406 mols of water charged initially to reactor

Time elapsed minutes	Reactor Pressure mm Hg	X mols	k_c'' liters$^{3/2}$/mol$^{3/2}$ min
0	318.0	0	---
2:00	328.4	0.00039	166
4:00	337.0	0.00072	161
6:00	344.5	0.00101	160
10:00	357.0	0.00149	159
14:00	367.0	0.00187	161
18:00	374.9	0.00217	162
22:00	381.0	0.00241	164
28:00	388.5	0.00270	168

Table 28. Calculation of k_c'' for a 2.5 order autocatalytic reaction. Run C-11. Temp. = 100.4°C

N_0 = 0.00340 mols of hydrazine and mols of oxygen charged initially to the reactor

N_{wo} = 0.00340 mols of water charged initially to reactor

Time elapsed minutes	Reactor Pressure mm Hg	X mols	k_c'' liters$^{3/2}$/mol$^{3/2}$ min
0	266.0	0	---
4:00	276.3	0.00039	124
6:00	281.0	0.00057	126
10:00	289.1	0.00088	125
16:00	299.8	0.00129	129
20:00	304.3	0.00146	125
32:00	316.2	0.00192	126
40:00	321.5	0.00212	126
48:00	325.8	0.00229	126

Table 29. Calculation of k_c'' for a 2.5 order autocatalytic reaction. Run C-13. Temp. = 99.6°C

N_O = 0.00348 mols of hydrazine and mols of oxygen charged initially to the reactor

N_{wo} = 0.00348 mols of water charged initially to reactor

Time elapsed minutes	Reactor Pressure mm Hg	X mols	k_c'' liters$^{3/2}$/mol$^{3/2}$ min
0	272.5	0	
3:00	281.2	0.00032	131
4:00	283.9	0.00042	131
6:00	288.8	0.00060	130
8:00	293.1	0.00077	130
10:00	297.3	0.00093	131
14:00	305.0	0.00122	134
16:00	308.2	0.00135	134
18:00	311.1	0.00146	135
28:00	323.2	0.00192	140

CONCLUDING DISCUSSION

A number of experiments were conducted on the thermal oxidation of hydrazine monohydrate in the vapor phase by oxygen in an effort to find a relationship which expresses the rate of reaction as a function of the concentration of the reactants. By use of the isolation technique, it was found that the rate of reaction is proportional to the concentration of hydrazine and to the concentration of oxygen, each to the first power. The results in the case where hydrazine monohydrate was isolated showed inconsistencies which indicated that some effect other than that of a simple homogeneous first order reaction had occurred. In an attempt to represent a number of runs as a homogeneous reaction of the second order (first order with respect to each of hydrazine and oxygen) it was seen that the values of the specific rate constant continuously increased as the reaction proceeded. This indicated that some component present was not being properly considered.

Several runs were made charging each of the products, nitrogen and water vapor, in excess. The runs in which water was charged in excess proceeded at a higher rate. An attempt was then made to determine the effect of the amount of water present upon the rate of reaction. Because the reaction rate and the specific rate constant, as calculated for a second order reaction, were the same function of the amount of water vapor present, it was possible to find the order of the reaction with respect to the water vapor concentration by means of graphical solution. The order with respect to water vapor was found to be between 0.4 and 0.5, but was taken as 0.5 so that the differential rate equation for the overall reaction could be directly integrated.

The actual reaction mechanism is perhaps much more complicated than the simple stoichiometric reactions which have been assumed; however, facilities were not available for carrying on an investigation of the reaction mechanism in detail.

NOMENCLATURE

a, b = constants

C = concentration, mols/liter

C_A = concentration of component A, mols/liter

C_B = concentration of component B, mols/liter

d = differential operator

k_c = specific rate constant for first order reaction, min^{-1}

k_c' = specific rate constant for second order reaction, liter/(mol)(min)

k_c'' = specific rate constant for 2.5 order autocatalytic reaction, $(\text{liter})^{3/2}/(\text{mol})^{3/2}(\text{min})$

n = number of gram mols

N_o = mols of reactant present in the reactor at the beginning of the reaction. Refers to either hydrazine or oxygen, or both in runs where equal amounts were charged.

N_{no} = mols of nitrogen present in the reactor at the beginning of the reaction.

N_{wo} = mols of water vapor present in the reactor at the beginning of the reaction.

P = pressure, mm Hg.

R = gas constant

t = time elapsed in minutes from beginning of reaction. Also designates temperature in $^{\circ}$C

T = temperature, $^{\circ}$K

V = volume, C.C.

X_o = mols of oxygen which have reacted at time t.

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