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THE HETEROGENEOUS DECOMPOSITION OF HYDRAZINE. PART 6. KINETICS OF THE DECOMPOSITION ON SUPPORTED PALLADIUM AND PLATINUM CATALYSTS

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THE HETEROGENEOUS DECOMPOSITION OF HYDRAZINE. PART 6. KINETICS OF THE DECOMPOSITION ON SUPPORTED PALLADIUM AND PLATINUM CATALYSTS

by

C.F. Sayer

SUMMARY

The decomposition of hydrazine on either a palladium or a platinum catalyst may be represented by the reaction

$$2N_2H_4 \rightarrow N_2 + H_2 + 2NH_3 \quad .$$

The observed one half order kinetics, changing to zero order with platinum, may be explained by deriving rate equations from the Langmuir adsorption isotherm and assuming that the initial, slow, step is the dissociative chemisorption of hydrazine in the form of NH_2 radicals. In accordance with the dual plane theory of Cosser and Tompkins it is suggested that the adsorption process and subsequent reaction occur only on the active sites of these metals.

Because these catalysts are much less active than a supported iridium catalyst neither is considered as an alternative for use in catalytic hydrazine thrusters.

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1 INTRODUCTION

Studies of the decomposition of hydrazine on supported iridium[1,2], rhodium[2,3] and ruthenium[4] catalysts have indicated two possible reactions:

$$3N_2H_4 \rightarrow N_2 + 4NH_3 \tag{1}$$

$$2N_2H_4 \rightarrow N_2 + H_2 + 2NH_3 \quad . \tag{2}$$

The decomposition on the rhodium catalyst follows reaction (2) and that on the iridium catalyst follows reaction (1), while on the ruthenium catalyst the overall decomposition reaction can be explained only by assuming that both reactions occur simultaneously.

The decomposition of hydrazine on the rhodium and ruthenium catalysts has been explained in terms of reaction mechanisms based on the dual plane theory of Cosser and Tompkins[5]. This theory postulates the existence of two types of surface site, the mode of adsorption of hydrazine depending on the type of site. One type is active for the dissociative adsorption of hydrazine in the form of NH_2 radicals, while on the second type hydrazine molecules are associatively adsorbed. The overall reaction appears to depend on the mode of adsorption.

The one half order kinetics observed for reaction (2) on the rhodium catalyst have been explained on the basis of the dissociative chemisorption of hydrazine on the active sites to form adsorbed NH_2 radicals. It was postulated that the next step was a Langmuir-Rideal reaction between adsorbed radicals, either NH_2 or NH, and a molecularly adsorbed hydrazine molecule to form the products. The Langmuir-Rideal reaction, involving a hydrazine molecule, was suggested as ^{15}N labelling experiments had shown that the two nitrogen atoms of one hydrazine molecule remain bonded together to form the nitrogen molecule[2].

On the ruthenium catalyst reaction (2) occurs following the dissociative chemisorption of hydrazine on the active sites as described for the rhodium catalyst. Reaction (1) also occurs on the second type of site on which hydrazine is associatively adsorbed to form an activated complex. This breaks down to yield ammonia and nitrogen in accordance with reaction (1).

It has not proved possible to establish a satisfactory mechanism consistent with the observed kinetics associated with the occurrence of reaction (1) for the decomposition of hydrazine on the iridium catalyst.

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This report describes the study of the kinetics of the decomposition of hydrazine on palladium and platinum catalysts and suggests mechanisms to account for the experimental data. The possibility of the use of either catalyst to replace the Shell 405 catalyst is assessed on the basis of their comparative catalytic activities.

2 EXPERIMENTAL

In all experiments propellant grade hydrazine of 97.7% w/w purity (obtained from Olin Mathieson Corporation, USA, to US Military Specification MIL-P-26536C) was used, diluted when necessary with demineralised water. The catalyst samples, obtained from Engelhard Industries Ltd, UK, in the form of ⅛ inch alumina pellets impregnated with 20% w/w of the appropriate metal, were used without further treatment.

The apparatus and experimental techniques were the same as those used to study the decomposition of hydrazine on the rhodium[3] and ruthenium[4] catalysts.

3 RESULTS AND DISCUSSION

3.1 The palladium catalyst

The composition of the permanent gas evolved on first contact of the catalyst with hydrazine and under various experimental conditions was determined by gas chromatography and the results are presented in Tables 1 to 4. The hydrogen content of the evolved permanent gas increased with respect to hydrazine concentration (Table 1) up to a limiting value of about 50% for high concentrations of hydrazine. The same limiting value was ultimately observed after a period of reaction time for concentrations of hydrazine which initially produced permanent gas containing only a small proportion of hydrogen. Equimolar quantities of hydrogen and nitrogen were found in the permanent gas evolved by the decomposition of 31.0 mole hydrazine dm^{-3} over the temperature range $15^{o}C$ to $45^{o}C$, and with catalyst samples pre-treated with ammonia or hydrogen at 1 bar.

The ratio of the number of moles of hydrazine decomposed to the number of moles of ammonia formed by the reaction was found, by titrimetric analysis, to average 1:1.07 for all the conditions of hydrazine concentration and temperature studied (Table 5).

The variation of the overall decomposition rate of hydrazine is shown in Fig. 1 as a function of the hydrazine concentration (see also Table 1). The variation of the rate of decomposition of 31.0 mole hydrazine dm^{-3} with respect to temperature is shown in Fig. 2 in the form of an Arrhenius plot, from which an activation energy of 44.6 ± 0.5 kJ mole^{-1} has been calculated.

The effects of the pre-adsorption of ammonia or hydrogen on the overall rate of decomposition of hydrazine were studied but the results were not reproducible. Only qualitative results could be obtained and these showed that both ammonia and hydrogen adsorbed on the catalyst at a pressure of 1 bar depress the overall decomposition rate to less than 30% of the rate observed using the untreated catalyst. However, with the ammonia pre-treated catalyst the decomposition rate increased with respect to time of reaction to reach a level similar to that observed using the standard catalyst, while the hydrogen pre-treated catalyst remained relatively inactive.

Most of the evidence obtained from the analysis of the products of the decomposition of hydrazine on the palladium catalyst indicates that only reaction (2) occurs, but the decomposition of low concentrations of hydrazine evolves permanent gas having stoichiometries between those corresponding to reactions (1) and (2). In this respect the results resemble those obtained with the ruthenium catalyst, from which it was postulated that reactions (1) and (2) occurred simultaneously. To determine the reaction occurring on the palladium catalyst the kinetic data must be analysed in terms of the two alternative schemes to establish which provides the most reasonable interpretation of all the experimental evidence.

First it is assumed that both reactions occur simultaneously. In this case all the hydrogen and an equal quantity of nitrogen are evolved by reaction (2) and the reaction rate may be calculated from the overall decomposition rate and the permanent gas composition from:

$$\text{rate of reaction (2)} = \frac{2 \times (\text{\% hydrogen in permanent gas}) \times (\text{overall rate})}{100} \quad .$$

The difference between the overall decomposition rate and the rate of reaction (2) is the rate of nitrogen evolution from reaction (1). The calculations of the rates of reactions (1) and (2) with respect to hydrazine concentration are given in Table 6 and the results are also shown in Fig. 3. The resulting kinetics appear rather complex and are not considered compatible with the dual plane theory as reaction (1) appears to be suppressed at high concentrations of hydrazine in favour of reaction (2). Because only reaction (2) appears to occur at high concentrations of hydrazine the Arrhenius plot in Fig. 2 refers solely to this reaction which therefore has an activation energy of 44.6 ± 0.5 kJ $mole^{-1}$.

If it is assumed that only reaction (2) occurs on the palladium catalyst, its rate is equal to the overall rate of reaction when the stoichiometry of the evolved permanent gas corresponds to that of reaction (2). However, before the kinetics may be analysed the observed non-stoichiometric composition of the permanent gas evolved under certain experimental conditions must be explained. Two possible explanations are:

(1) the low hydrogen content of the evolved permanent gas results from some mechanism reducing the evolution of hydrogen formed at the catalyst surface;

(2) the low hydrogen content is caused by the evolution of nitrogen in addition to that from reaction (2).

The second possibility is discounted because the only source of nitrogen, apart from hydrazine, is the ammonia formed by the decomposition of hydrazine and liberation of nitrogen from this source would also involve the liberation of three times as much hydrogen. The readiness with which palladium adsorbs hydrogen is well documented[6] and in view of the effect of (a) the pre-adsorption of hydrogen on the catalyst, and (b) the time of reaction, in changing the stoichiometry of the evolved permanent gas, it is postulated that the mechanism which reduces the evolution of hydrogen is adsorption on the surface of the palladium catalyst. This phenomenon is only observed, in the form of the non-stoichiometric composition of the evolved permanent gas, when the reaction rate is low and the catalyst surface is only sparsely covered by adsorbed species. Both conditions apply only to the use of a low concentration of hydrazine with the untreated catalyst. As the reaction proceeds hydrogen and ammonia are adsorbed on the catalyst surface covering vacant sites until the surface is saturated with adsorbed species, after which all the hydrogen produced by the reaction is contained in the evolved permanent gas. Pre-treatment of the catalyst with ammonia or hydrogen reduces the number of vacant sites, thereby reducing the decomposition rate of hydrazine and causing all the hydrogen formed during decomposition to be present in the evolved permanent gas. It has been suggested that ammonia is only weakly adsorbed on the iridium catalyst[7] and that in the presence of liquid hydrazine the adsorbed ammonia molecules are slowly replaced by hydrazine molecules. This applies also to the palladium catalyst, with which the decomposition rate using the ammonia pre-treated catalyst slowly increases with respect to reaction time to reach a level similar to that observed with the untreated catalyst. The hydrogen pre-treated catalyst remains relatively inactive showing that hydrogen is more strongly adsorbed and is not replaced by hydrazine molecules under the particular experimental conditions.

Assuming the occurrence of only reaction (2) and the partial adsorption of hydrogen, the rate of reaction (2) may be calculated only from the available data as twice the rate of evolution of nitrogen, and these calculations are given in Table 7. The rate of reaction, R, and the concentration of reactant, c, may be related by

$$R = k c^n$$

where k is the rate constant and n is the order of reaction. Taking logs:

$$\log_{10} R = \log_{10} k + n \log_{10} c$$

Fig. 4 presents the data of Table 7 in the form of $\log_{10} R$ plotted with respect to $\log_{10} c$. The slope of the straight line plot, and hence the order of reaction, is approximately one half. The activation energy of 44.6 ± 0.5 kJ mole^{-1} calculated from Fig. 2 refers to reaction (2) as the composition of the evolved permanent gas corresponds to the stoichiometry of this reaction. However, the rate equation for a one half order reaction derived[3] from the Langmuir adsorption isotherm is

$$R = k K^{\frac{1}{2}} c^{\frac{1}{2}}$$

and because both the equilibrium constant for the adsorption process, K, and the reaction rate constant, k, are temperature dependent the calculated activation energy does not refer solely to reaction (2) and is therefore only an apparent value.

The most rational interpretation of all the experimental data is considered to be a reaction scheme involving only reaction (2) with the assumption that under certain conditions adsorption of hydrogen on the catalyst surface changes the stoichiometry of the evolved permanent gas.

It is postulated that the initial step in the reaction mechanism is the dissociative chemisorption of hydrazine molecules in the form of NH_2 radicals on the active sites of the palladium catalyst. For such a case the use of the

Langmuir adsorption isotherm to derive the rate equation predicts one half order kinetics for sparse surface coverage by adsorbed radicals changing to zero order kinetics when the surface is saturated. As the observed kinetics are one half order over the entire hydrazine concentration range the palladium catalyst surface is never saturated and the initial adsorption step is rate-controlling. It is suggested, by analogy with the rhodium and ruthenium catalysts, that a Langmuir-Rideal reaction then occurs between adsorbed radicals, either NH_2 or NH, and a molecularly adsorbed hydrazine molecule to form the products. However, in the absence of any data from ^{15}N labelling experiments it is only a tentative suggestion for the final steps.

3.2 The platinum catalyst

The results obtained with the platinum catalyst are qualitatively similar to those with the palladium catalyst and only differences between the two systems are discussed in detail.

The analyses of the evolved permanent gas (see Tables 8 to 11) showed the same trend to a limiting composition of equimolar quantities of hydrogen and nitrogen as observed with the palladium catalyst. However, this limiting composition is reached at lower concentrations of hydrazine than with the palladium catalyst. The titrimetric analysis showed that the decomposition of each mole of hydrazine was accompanied on average by the production of 0.97 mole of ammonia (see Table 12).

The analysis of the evolved permanent gas indicated the occurrence of only reaction (2) more conclusively than the results with the palladium catalyst and reaction (2) is therefore assumed to account for the decomposition of hydrazine on the platinum catalyst. The divergence from the reaction stoichiometry of the permanent gas evolved from low concentrations of hydrazine is again assumed to result from the adsorption of hydrogen on the catalyst surface. The overall decomposition rate is shown in Fig. 5 to be a decreasing function of the hydrazine concentration, becoming almost independent at high concentrations (see also Table 8). Calculation of the rate of reaction (2) from the rate of nitrogen evolution (see Table 13) produces the data plotted in log-log form in Fig. 6. This shows that at low concentrations of hydrazine the order of reaction is approximately one half, decreasing to zero for concentrations in excess of 25 mole hydrazine dm^{-3}. It was noted in the previous section that rate equations consistent with such a change in observed kinetics could be derived from the Langmuir adsorption isotherm, assuming the dissociative chemisorption of hydrazine molecules in the form of NH_2 radicals. The rate equation for the one half order region has been given for the palladium catalyst. The rate equation for the zero order kinetics for high concentrations of hydrazine on the platinum catalyst is:

$$R = k \quad .$$

The variation with temperature of the rate of decomposition of hydrazine on the platinum catalyst has been studied using 30.8 mole hydrazine dm^{-3}. For this concentration the zero order rate equation applies and as the only temperature dependent term is the reaction rate constant the activation energy of 32.2 ± 0.4 kJ $mole^{-1}$, calculated from the Arrhenius plot in Fig. 7, refers to reaction (2).

It is postulated that the reaction mechanism for the decomposition of hydrazine on the platinum catalyst is the same as that described for reaction (2) on the palladium catalyst.

3.3 Choice of active metal for hydrazine decomposition catalysts

The heterogeneous decomposition of hydrazine has been studied using five supported metal catalysts. The order of catalytic activity with respect to the decomposition of 31.0 mole hydrazine dm^{-3} (98.4% w/w) at 22 ± 2°C is

$$Ir >> Ru > Rh \ , \ Pd \ , \ Pt \quad .$$

Because iridium is at least thirty times as active as the other metals, it is considered that only supported iridium catalysts will find application in small hydrazine thrusters operating under cold start conditions.

4 CONCLUSIONS

The decomposition of hydrazine on either a palladium or a platinum catalyst may be represented by the reaction

$$2N_2H_4 \rightarrow N_2 + H_2 + 2NH_3 \quad .$$

Under certain experimental conditions the evolved permanent gas was non-stoichiometric as a result of the adsorption of hydrogen on the catalyst surface.

It is postulated that the initial step in the reaction is the dissociative chemisorption of hydrogen molecules in the form of NH_2 radicals on the active sites of these catalysts. On this assumption the Langmuir adsorption isotherm may be used to derive rate equations which are consistent with the observed one half order kinetics, changing to zero order on the platinum catalyst. It has been tentatively suggested that a Langmuir-Rideal reaction occurs between adsorbed radicals, either NH_2 or NH, and a molecularly adsorbed hydrazine molecule to form the products.

From the results of laboratory scale testing of the catalytic activity of five supported platinum group metal catalysts it is concluded that only the iridium catalyst is suitable for catalytic hydrazine thruster applications requiring cold starts.

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TABLE 1

Variation of the composition of the evolved permanent gas and the overall decomposition rate with respect to hydrazine concentration using the supported palladium catalyst at 24°C

Hydrazine concentration mole dm^{-3}	Permanent gas composition		Overall decomposition rate $\frac{d[N_2 + H_2]}{dt}$ mole g^{-1}s^{-1} × 10^6
	% H_2	% N_2	
1.2	7.0	93.0	2.0
3.1	12.3	87.7	3.4
4.8	16.2	83.8	4.5
6.1	20.1	79.9	5.0
9.3	32.0	68.0	7.9
12.3	36.0	64.0	9.9
16.5	40.5	59.5	10.9
18.8	45.0	55.0	12.9
23.0	47.0	53.0	16.2
28.3	47.5	52.5	17.8
31.0	53.0	47.0	22.2

TABLE 2

Variation of the composition of the evolved permanent gas and the overall decomposition rate with respect to temperature for the decomposition of 31.0 mole hydrazine dm^{-3} on the supported palladium catalyst

Temperature		1/K × 10^3	Permanent gas composition		Overall decomposition rate $\frac{d[N_2 + H_2]}{dt}$ mole g^{-1}s^{-1} × 10^6	6 + log$_{10}$ rate
°C	K		% H_2	% N_2		
15.0	288.2	3.470	48.5	51.5	13.6	1.134
19.0	292.2	3.422	49.5	50.5	18.2	1.260
22.0	295.2	3.388	53.0	47.0	20.8	1.318
24.6	297.8	3.358	49.0	51.0	22.9	1.360
30.0	303.2	3.298	48.6	51.4	33.9	1.530
34.5	307.7	3.250	50.9	49.1	44.4	1.647
40.0	313.2	3.193	51.3	48.7	60.8	1.784
45.0	318.2	3.143	49.1	50.9	81.8	1.913

TABLE 3

The effect of hydrogen pre-adsorption on the supported palladium catalyst on the composition of the evolved permanent gas

Hydrogen pre-adsorbed	Hydrazine concentration mole dm^{-3}	Temperature ^{o}C	Permanent gas composition	
			% H_2	% N_2
No	3.1	24.0	12.3	87.7
Yes	3.1	24.0	48.4	51.6
No	3.1	41.0	21.3	78.7
Yes	3.1	41.0	50.3	49.7
No	3.1	10.0	9.8	90.2
Yes	3.1	10.0	47.7	52.3
No	9.3	24.0	32.0	68.0
Yes	9.3	24.0	51.1	48.9
No	18.8	24.0	45.0	55.0
Yes	18.8	24.0	49.1	50.9
No	31.0	24.0	53.0	47.0
Yes	31.0	24.0	48.6	51.4

TABLE 4

The effect of ammonia pre-adsorption on the supported palladium catalyst on the composition of the evolved permanent gas

Ammonia pre-adsorbed	Hydrazine concentration mole dm^{-3}	Temperature ^{o}C	Permanent gas composition	
			% H_2	% N_2
No	3.1	10.0	9.8	90.2
Yes	3.1	10.0	46.3	53.7
No	3.1	24.0	12.3	87.7
Yes	3.1	24.0	51.9	48.1
No	3.1	41.0	21.3	78.7
Yes	3.1	41.0	47.9	52.1
No	9.3	24.0	32.0	68.0
Yes	9.3	24.0	48.1	51.9
No	18.8	24.0	45.0	55.0
Yes	18.8	24.0	50.6	49.4

TABLE 5

Variation of the hydrazine to ammonia conversion ratio with respect to hydrazine concentration and temperature for the palladium catalyst

Hydrazine concentration mole dm^{-3}	Temperature ^{o}C	$N_2H_4 : NH_3$ ratio
3.1	24.0	1 : 1.07
9.3	24.0	1 : 1.01
18.8	24.0	1 : 1.10
9.3	10.0	1 : 1.07
9.3	34.0	1 : 1.09

TABLE 6

Calculation of the rates of reactions (1) and (2) from the overall rate of reaction

Hydrazine concentration mole dm^{-3}	Overall rate of reaction $\frac{d[N_2 + H_2]}{dt}$ mole gm^{-1} sec^{-1} × 10^6	% H_2 in permanent gas	% of overall reaction due to reaction (2)	Rate of reaction (2) $\frac{d[N_2 + H_2]}{dt}$ mole gm^{-1} sec^{-1} × 10^6	Rate of reaction (2) $-\frac{d[N_2H_4]}{dt}$ mole gm^{-1} sec^{-1} × 10^6	Rate of reaction (1) $\frac{d[N_2]}{dt}$ mole gm^{-1} sec^{-1} × 10^6	Rate of reaction (1) $-\frac{d[N_2H_4]}{dt}$ mole gm^{-1} sec^{-1} × 10^6
1.2	2.0	7	14.0	0.28	0.28	1.72	0.57
3.1	3.4	12.3	24.6	0.84	0.84	2.56	0.85
4.8	4.5	16.2	32.4	1.46	1.46	3.04	1.01
6.1	5.0	20.1	40.2	2.0	2.0	3.0	1.0
9.3	7.9	32.0	64.0	5.1	5.1	2.8	0.93
12.3	9.9	36.0	72.0	7.1	7.1	2.8	0.93
16.5	10.9	40.5	81.0	8.8	8.8	2.1	0.7
18.8	12.9	45.0	90.0	11.6	11.6	1.3	0.43
23.0	16.2	47.0	94.0	15.0	15.0	1.2	0.40
28.3	17.8	47.5	95.0	16.9	16.9	0.9	0.30
31.0	22.2	53.0	106.0	23.5	23.5	-	-

TABLE 7

Calculation of the rate of reaction (2) for the decomposition of hydrazine on the supported palladium catalyst

Hydrazine concentration mole dm^{-3}	Overall rate of reaction $\frac{d[N_2 + H_2]}{dt}$ mole gm^{-1} sec^{-1} × 10^6	% N_2 in permanent gas	Rate of nitrogen evolution $\frac{d[N_2]}{dt}$ mole gm^{-1} sec^{-1} × 10^6	Rate of reaction (2) $-\frac{d[N_2H_4]}{dt}$ mole gm^{-1} sec^{-1} × 10^6	$\log_{10}$ hydrazine concentration	6 + $\log_{10}$ rate of reaction (2)
1.2	2.0	93.0	1.86	3.72	0.079	0.571
3.1	3.4	87.7	3.0	6.0	0.491	0.776
4.8	4.5	83.8	3.8	7.5	0.681	0.877
6.1	5.0	79.9	4.0	8.0	0.785	0.903
9.3	7.9	68.0	5.4	10.7	0.968	1.031
12.3	9.9	64.0	6.3	12.7	1.090	1.103
16.5	10.9	59.5	6.5	13.0	1.217	1.113
18.8	12.9	55.0	7.1	14.2	1.274	1.152
23.0	16.2	53.0	8.6	17.2	1.362	1.235
28.3	17.8	52.5	9.3	18.7	1.452	1.272
31.0	22.2	47.0	10.4	20.9	1.491	1.319

TABLE 8

Variation of the composition of the evolved permanent gas and the overall decomposition rate with respect to hydrazine concentration using the supported platinum catalyst at 24°C

Hydrazine concentration mole dm^{-3}	Permanent gas composition		Overall decomposition rate $\frac{d[N_2 + H_2]}{dt}$ mole $g^{-1}s^{-1}$ × 10^6
	% H_2	% N_2	
0.6	8.0	92.0	4.38
1.2	16.5	83.5	6.59
3.1	31.0	69.0	11.9
4.7	39.0	61.0	16.1
6.3	44.5	55.5	19.3
9.4	50.0	50.0	26.0
12.5	51.2	48.8	29.7
15.6	50.5	49.5	31.3
19.4	48.5	51.5	33.0
21.8	50.7	49.3	34.5
25.6	49.2	50.8	35.0
28.1	48.3	51.7	34.8
30.8	51.1	48.9	36.4

TABLE 9

Variation of the overall decomposition rate and the composition of the evolved permanent gas with respect to temperature for the decomposition of 30.8 mole hydrazine dm^{-3} on the supported platinum catalyst

Temperature		1/K × 10^3	Permanent gas composition		Overall decomposition rate $\frac{d[N_2 + H_2]}{dt}$ mole $g^{-1}s^{-1}$ × 10^6	6 + $\log_{10}$ rate
°C	K		% H_2	% N_2		
15.0	288.2	3.470	48.2	51.8	23.0	1.362
20.0	293.2	3.411	50.6	49.4	29.0	1.462
25.0	298.2	3.353	51.1	48.9	35.5	1.550
29.8	303.0	3.300	50.7	49.3	41.5	1.618
34.2	307.4	3.253	49.9	50.1	54.0	1.732
40.0	313.2	3.193	51.1	48.9	63.1	1.800
45.8	319.0	3.153	53.0	47.0	79.5	1.900
53.5	326.7	3.061	49.1	50.9	110.0	2.041
58.8	332.0	3.012	47.9	52.1	132.0	2.121

TABLE 10

The effect of hydrogen pre-adsorption on the supported platinum catalyst on the composition of the evolved permanent gas

Hydrogen pre-adsorbed	Hydrazine concentration mole dm^{-3}	Temperature ^{o}C	Permanent gas composition	
			% H_2	% N_2
No	1.2	10	11.3	88.7
Yes	1.2	10	48.2	51.8
No	1.2	25	16.5	83.5
Yes	1.2	25	50.7	49.3
No	1.2	40	17.0	83.0
Yes	1.2	40	50.1	49.9
No	4.7	25	39.0	61.0
Yes	4.7	25	49.1	50.9
No	25.6	25	49.2	50.8
Yes	25.6	25	51.3	48.7

TABLE 11

The effect of ammonia pre-adsorption on the supported platinum catalyst on the composition of the evolved permanent gas

Ammonia pre-adsorbed	Hydrazine concentration mole dm^{-3}	Temperature ^{o}C	Permanent gas composition	
			% H_2	% N_2
No	1.2	10	11.3	88.7
Yes	1.2	10	51.3	48.7
No	1.2	25	16.5	83.5
Yes	1.2	25	52.4	47.6
No	1.2	40	17.0	83.0
Yes	1.2	40	47.1	52.9
No	4.7	25	39.0	61.0
Yes	4.7	25	47.9	52.1
No	25.6	25	49.2	50.8
Yes	25.6	25	49.1	50.9

TABLE 12

Variation of the hydrazine to ammonia conversion ratio with respect to hydrazine concentration and temperature for the platinum catalyst

Hydrazine concentration mole dm^{-3}	Temperature ^{o}C	N_2H_4 : NH_3 ratio
3.1	24.0	1 : 0.97
9.3	24.0	1 : 0.94
18.8	24.0	1 : 1.01
9.3	10.0	1 : 0.98
9.3	34.0	1 : 0.96

<u>TABLE 13</u>

Calculation of the rate of reaction (2) for the decomposition of hydrazine on the supported platinum catalyst

Hydrazine concentration mole dm^{-3}	Overall rate of reaction $\frac{d[N_2 + H_4]}{dt}$ mole gm^{-1} sec^{-1} × 10^6	% nitrogen in permanent gas	Rate of nitrogen formation $\frac{d[N_2]}{dt}$ mole gm^{-1} sec^{-1} × 10^6	Rate of reaction (2) $-\frac{d[N_2H_4]}{dt}$ mole gm^{-1} sec^{-1} × 10^6	$\log_{10}$ hydrazine concentration	6 + $\log_{10}$ rate of reaction (2)
0.62	4.38	92.0	4.0	8.1	-0.208	0.906
1.2	6.59	83.5	5.5	11.0	0.079	1.042
3.1	11.9	69.0	8.2	16.4	0.491	1.215
4.7	16.1	61.0	9.8	19.6	0.672	1.293
6.3	19.3	55.5	10.7	21.4	0.799	1.331
9.4	26.0	50.0	13.0	26.0	0.973	1.415
12.5	29.7	48.8	14.5	29.0	1.097	1.462
15.6	31.3	49.5	15.5	31.0	1.193	1.491
19.4	33.0	51.5	17.0	34.0	1.288	1.531
21.8	34.5	49.3	17.0	34.0	1.338	1.531
25.6	35.0	50.8	17.8	35.6	1.408	1.551
28.1	34.8	51.7	18.0	36.0	1.449	1.556
30.8	36.4	48.9	17.8	35.6	1.489	1.551

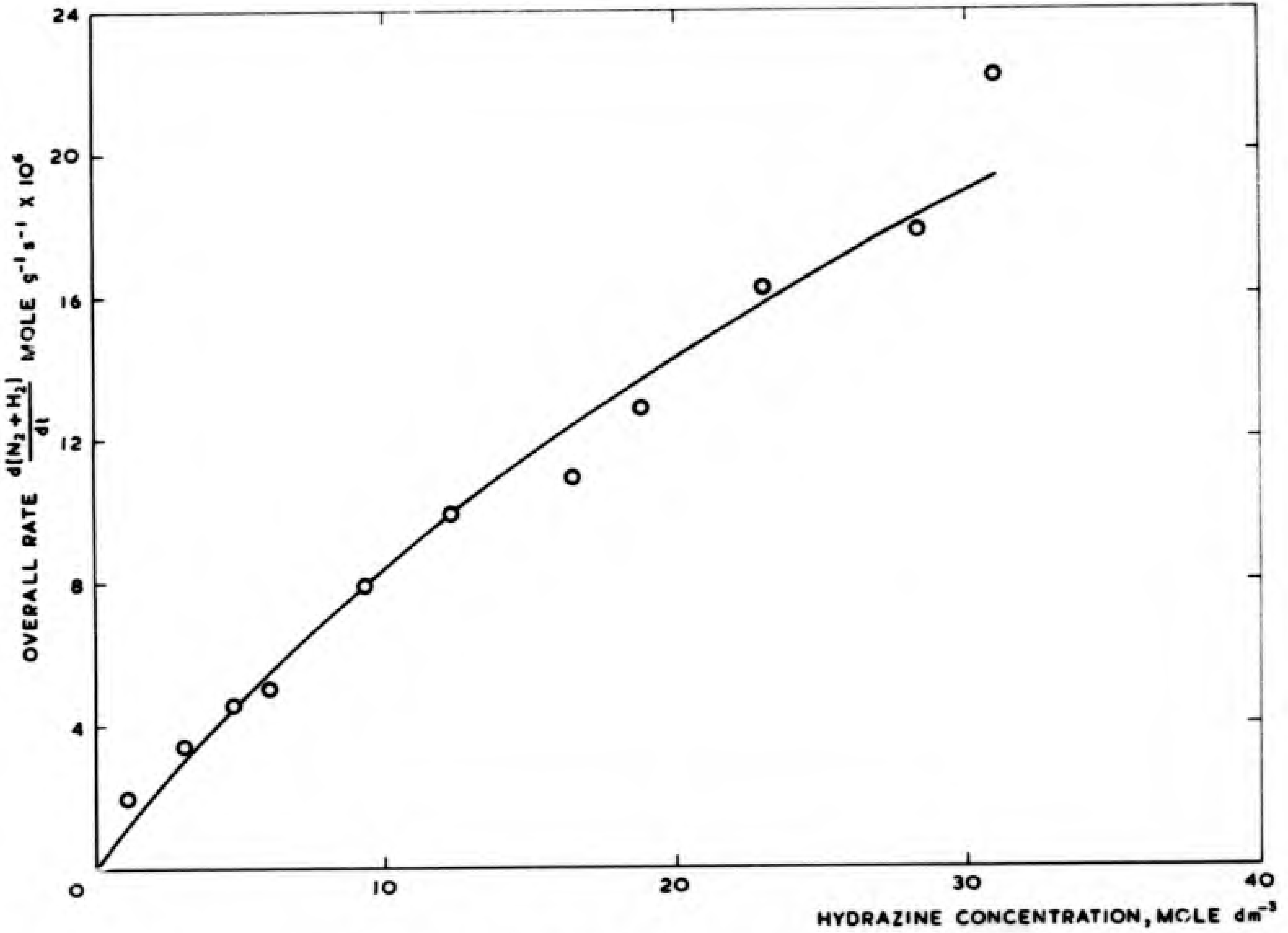

FIG. I OVERALL DECOMPOSITION RATE OF HYDRAZINE ON THE SUPPORTED PALLADIUM CATALYST AT 24°C WITH RESPECT TO HYDRAZINE CONCENTRATION

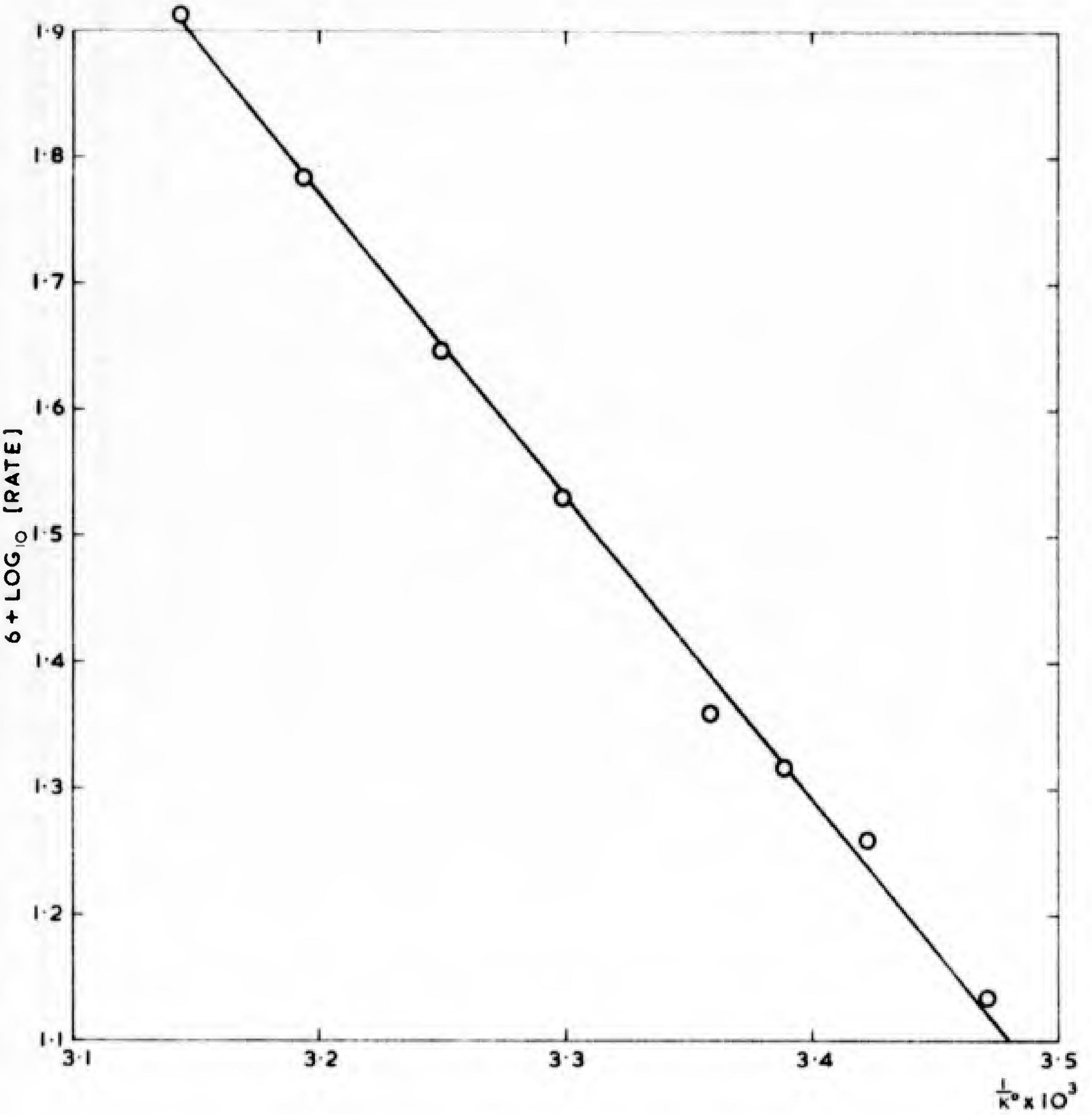

FIG. 2 ARRHENIUS PLOT FOR THE DECOMPOSITION OF 31·0 MOLE HYDRAZINE, dm^{-3} ON THE PALLADIUM CATALYST

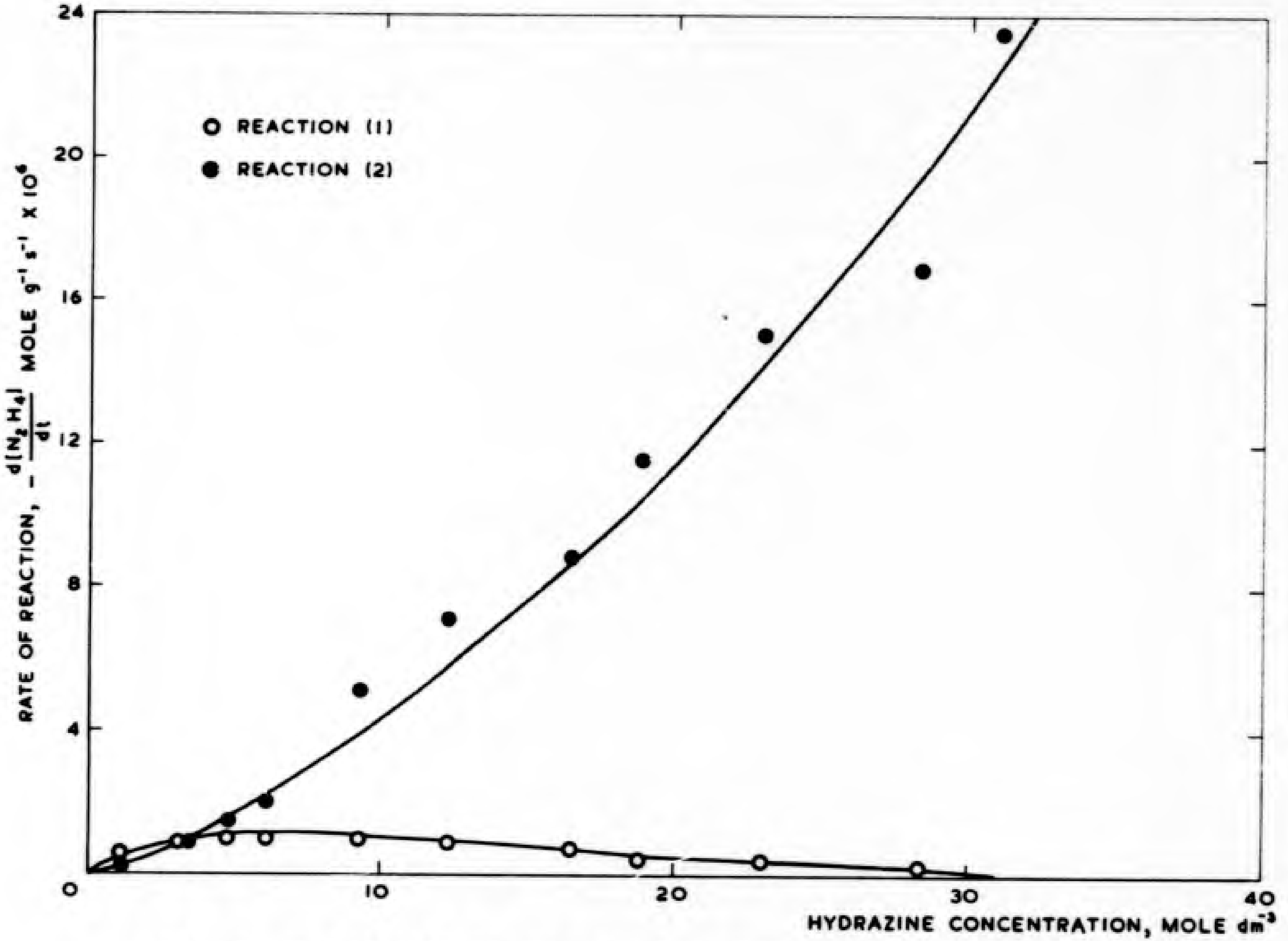

FIG. 3 VARIATION OF THE CALCULATED RATES OF REACTIONS (1) AND (2) ON THE SUPPORTED PALLADIUM CATALYST AT 24°C WITH RESPECT TO HYDRAZINE CONCENTRATION

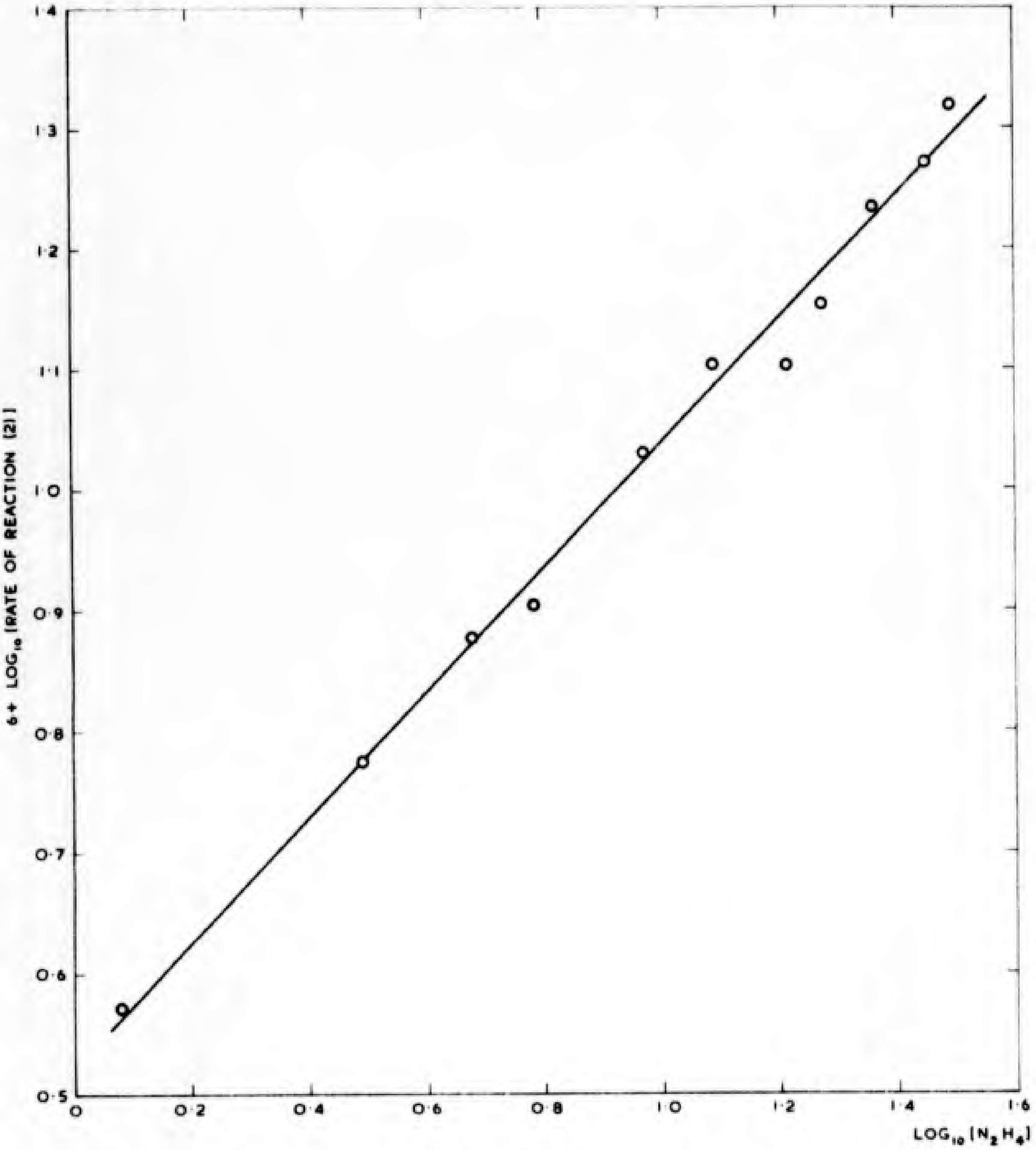

FIG. 4 LOG PLOT OF THE VARIATION OF THE RATE OF REACTION (2) ON THE PALLADIUM CATALYST AT 24°C WITH RESPECT TO HYDRAZINE CONCENTRATION

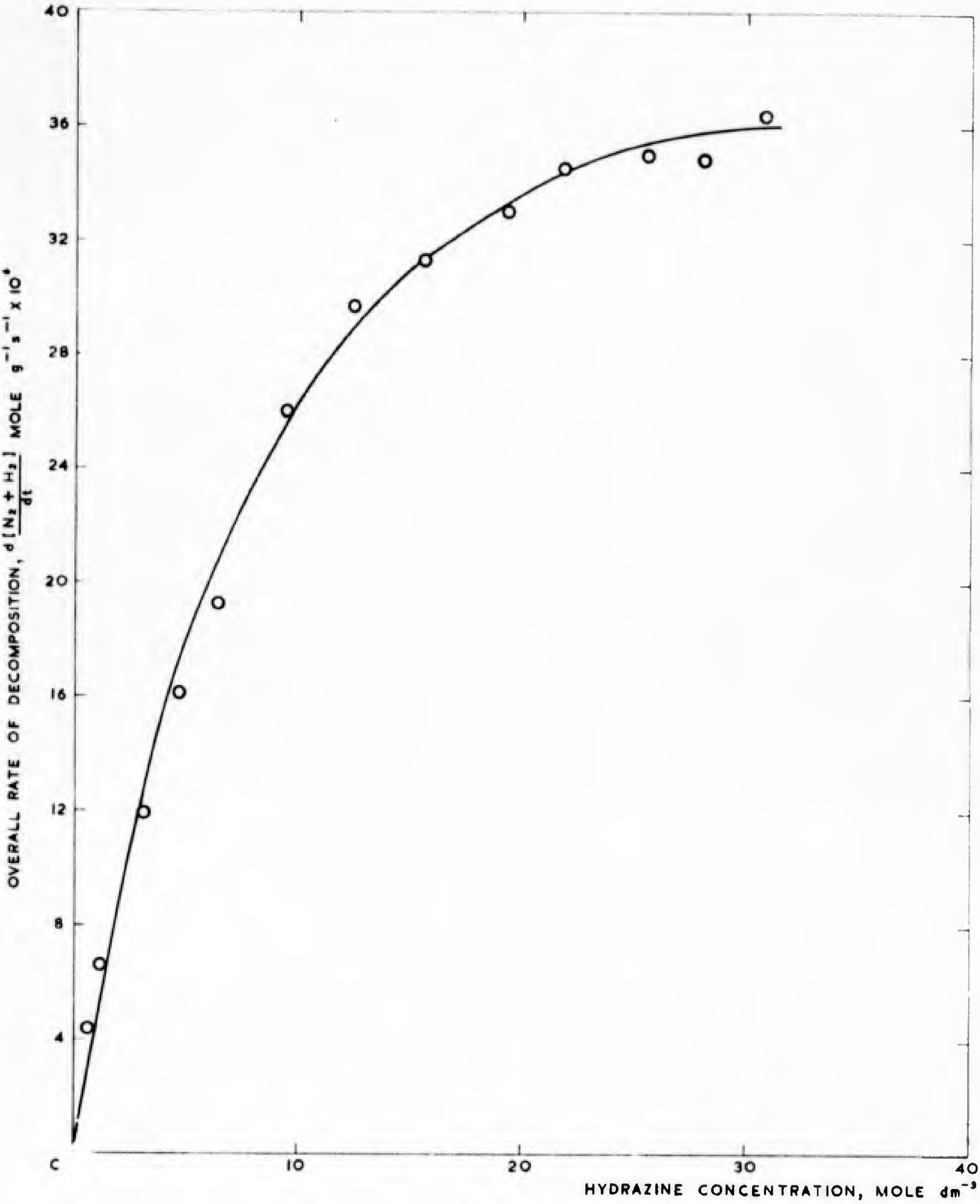

FIG. 5 VARIATION OF THE OVERALL DECOMPOSITION RATE OF HYDRAZINE ON THE SUPPORTED PLATINUM CATALYST AT 24 °C WITH RESPECT TO HYDRAZINE CONCENTRATION

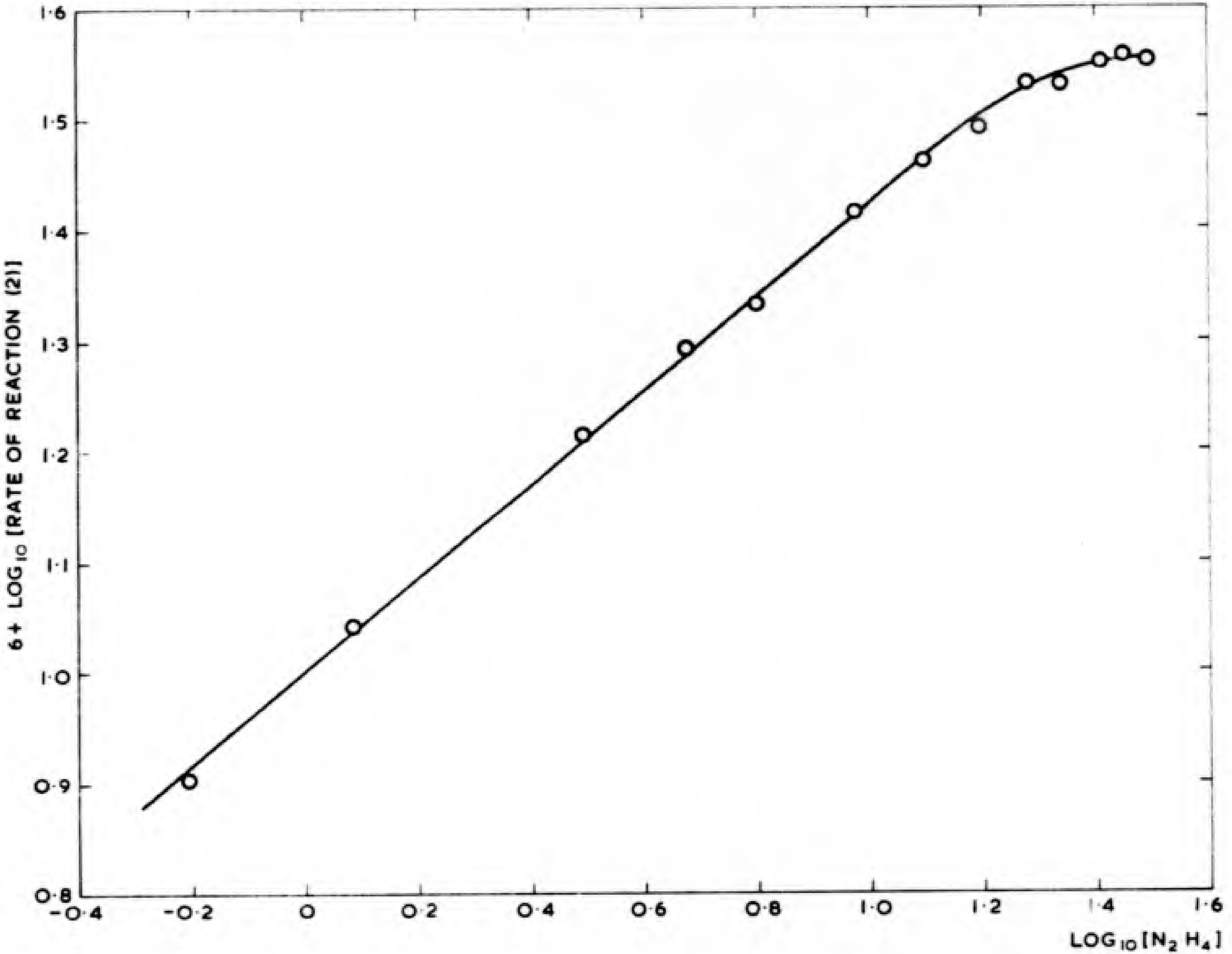

FIG. 6 LOG PLOT OF THE VARIATION OF THE RATE OF REACTION (2) ON THE SUPPORTED PLATINUM CATALYST AT 24°C WITH RESPECT TO HYDRAZINE CONCENTRATION

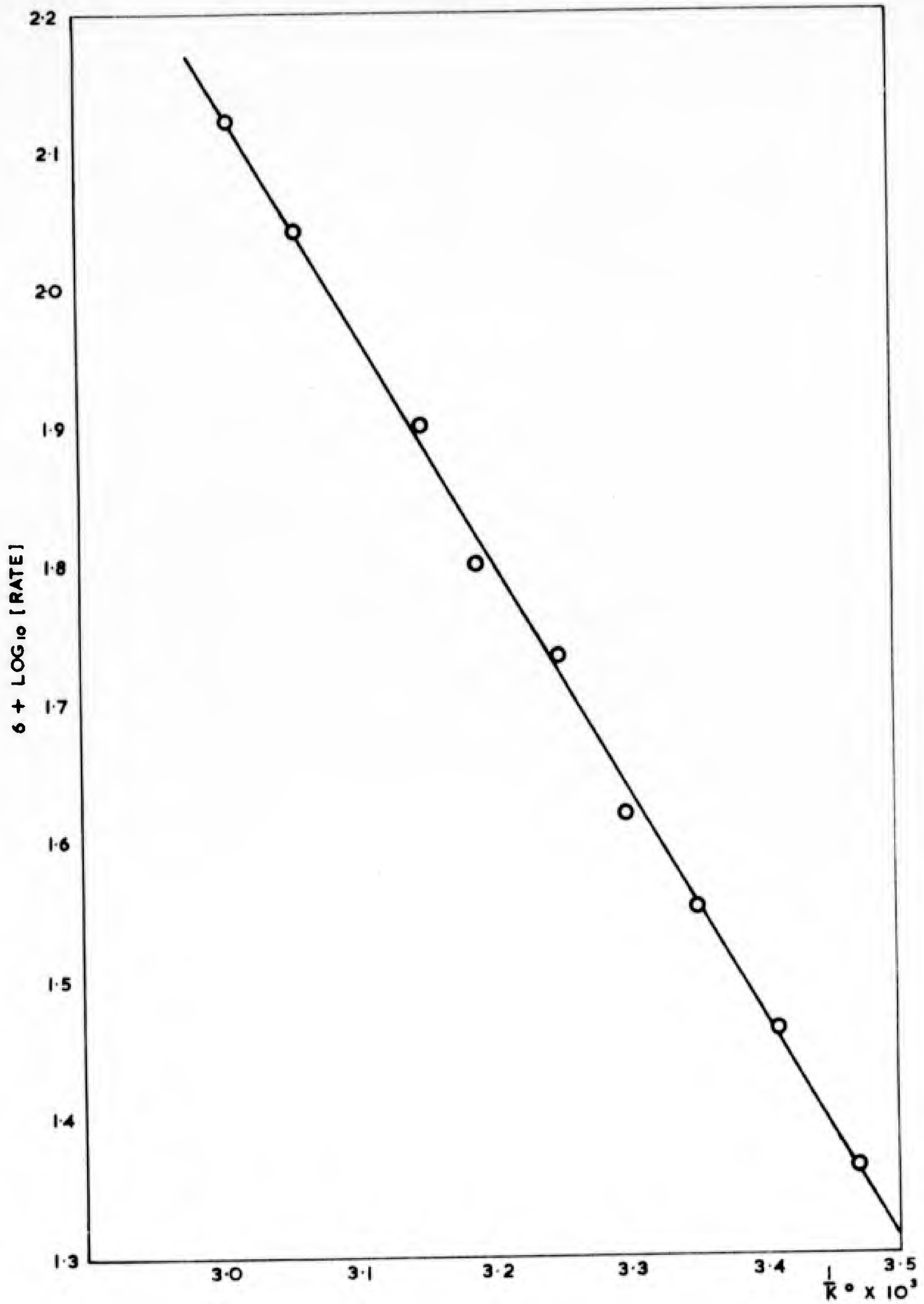

FIG. 7 ARRHENIUS PLOT FOR THE DECOMPOSITION OF 30·8 MOLE HYDRAZINE, dm^{-3} ON THE SUPPORTED PLATINUM CATALYST