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THE HETEROGENEOUS DECOMPOSITION OF
HYDRAZINE. PART 4. THE KINETICS OF
THE DECOMPOSITION OF LIQUID HYDRAZINE
ON A SUPPORTED RHODIUM CATALYST

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November 1971

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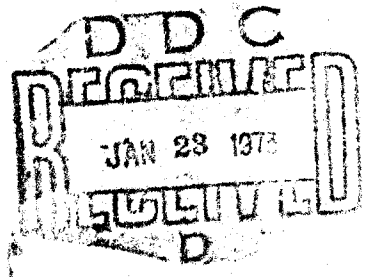
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OF HYDRAZINE:
PART 4. THE KINETICS OF THE DECOMPOSITION
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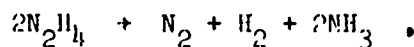
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SUMMARY

The kinetics of the decomposition of liquid hydrazine on a supported rhodium catalyst exhibit a change from half order for low concentrations of hydrazine to zero order for high concentrations of hydrazine.

The reaction follows the stoichiometry



the activation energy of the process being $41,300 \pm 340 \text{ J mole}^{-1}$ ($9,876 \pm 81 \text{ cal mole}^{-1}$).

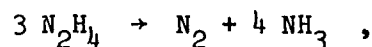
The observed kinetics have been explained by deriving the rate equations from the Langmuir adsorption isotherm on the assumption that the hydrazine molecules are dissociatively adsorbed as NH_2' radicals. A mechanism is postulated which involves a Langmuir-Rideal type of reaction between adsorbed radicals and a liquid phase hydrazine molecule.

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1 INTRODUCTION

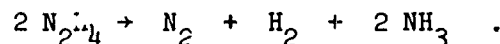
The kinetics of the decomposition of liquid hydrazine on a supported iridium catalyst (Shell 405 catalyst) have been studied and the reaction was found to be first order with respect to hydrazine concentration over the range 15-100% w/w hydrazine. The activation energy for the reaction was calculated to be $65,400 \pm 90 \text{ J mole}^{-1}$ ($15,628 \pm 22 \text{ cal mole}^{-1}$). Analysis of the products of the decomposition reaction^{1,2} by gas chromatography and titrimetric methods showed that the decomposition may be represented by the reaction



hydrogen being present only in trace quantities.

Mass spectrometric analysis of the nitrogen produced by the catalytic decomposition of hydrazine enriched with N^{15} in the presence of a large excess of normal hydrazine has shown that the nitrogen molecule is formed from the two nitrogen atoms of one hydrazine molecule without nitrogen-nitrogen bond fission.

In addition to iridium other platinum group metals have been considered for the catalytic decomposition of hydrazine³. The use of a supported rhodium catalyst produces nitrogen, hydrogen and ammonia in relative quantities different from those produced by the supported iridium catalyst². On the rhodium catalyst the rate of decomposition of hydrazine is much lower than on the iridium catalyst and may be represented by the reaction



The use of N^{15} as a tracer showed that the nitrogen molecule is again formed from the two nitrogen atoms of one hydrazine molecule without nitrogen-nitrogen bond fission.

This report describes the investigation of the kinetics of the decomposition of liquid hydrazine on a supported rhodium catalyst and, in accordance with recent findings on the decomposition of hydrazine vapour on metal films^{4,5}, a reaction mechanism is postulated.

2 EXPERIMENTAL

In all experiments propellant grade hydrazine of 97.7% w/w concentration (obtained from the Olin Mathieson Corp. USA, and conforming to US Military Specification MIL-P26536B⁶) was used, diluted when necessary with demineralised water. The concentrations of the resulting solutions were determined by measurement of their refractive indices⁷. The catalyst sample obtained from Engelhard Industries Ltd., Cinderford, Gloucestershire, was in the form of 1/8 inch alumina pellets (1/8 inch diameter by 1/8 inch length) impregnated with 20% rhodium.

The apparatus used to study the kinetics of the decomposition of liquid hydrazine on the supported rhodium catalyst is shown in Fig. 1. 50 ml of hydrazine solution was placed in the reaction vessel and the catalyst pellets were placed in the side arm. The apparatus was then immersed in a thermostatically controlled water bath and allowed to reach equilibrium temperature. The catalyst pellets were dropped into the solution by rotating the side arm through 180° and the volume of gas produced by the decomposition reaction was measured at regular intervals of time at atmospheric pressure by means of a gas burette. As all traces of ammonia were removed by a molecular sieve filter the gas consisted of equimolar quantities of nitrogen and hydrogen. The rate of reaction was calculated from the volume of gas produced in unit time and expressed in moles of hydrazine decomposed per unit mass of catalyst per unit of time. The rates were essentially independent of time.

3 RESULTS

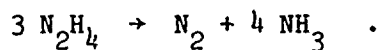
Fig. 2 shows the variation of the rate of decomposition of hydrazine on the supported rhodium catalyst at 21°C with respect to hydrazine concentration. The rate of decomposition increases rapidly with respect to hydrazine concentration up to 20% w/w and then starts to level out, the rate of decomposition becoming independent of hydrazine concentration over the range 50-100% w/w hydrazine.

The effect of temperature over the range 4 to 48°C on the rate of decomposition of 72.7% w/w hydrazine solution on the supported rhodium catalyst is shown in Fig. 3 in the form of an Arrhenius plot.

4 DISCUSSION

Recent papers^{4,5} on the decomposition of hydrazine vapour on tungsten and molybdenum films have shown that the chemisorption of hydrazine may occur in two ways. The associative chemisorption of hydrazine molecules to a single surface atom may occur and the activated complex so formed then breaks down to

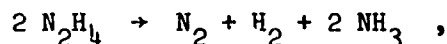
form nitrogen and ammonia, as may be represented by the reaction



The second mode of adsorption is the dissociative chemisorption of one hydrazine molecule to form two NH_2 radicals on two surface sites. These adsorbed radicals then undergo further surface dissociation to produce NH , N and H as adsorbed species. The adsorbed hydrogen atoms combine and desorb as hydrogen gas whereas the nitrogen atoms remain adsorbed on the surface site due to the strong metal-nitrogen bond.

The N-N bond in hydrazine is weaker than the H-H bond in hydrogen which in turn is weaker than the N-N bond in nitrogen. Therefore any metal which is capable of the dissociative chemisorption of nitrogen will be effective for the dissociative chemisorption of hydrazine and the formation of hydrogen and adsorbed nitrogen atoms. On the other hand, any metal which is capable of the dissociative adsorption of hydrogen, but not nitrogen, will dissociatively chemisorb N_2H_4 as NH_2 radicals, but the extent of further dissociation is limited to the species NH and H . Rhodium⁴ is one such metal.

Turning now to consider the decomposition of hydrazine on a supported rhodium catalyst, it has been shown² that the decomposition may be represented by the reaction



and the nitrogen molecule so formed is produced from the two nitrogen atoms of one hydrazine molecule without nitrogen-nitrogen bond fission. As the reaction stoichiometry is different from that for the decomposition of hydrazine following associative chemisorption on both tungsten and molybdenum it may indicate that one step in the reaction is the dissociative chemisorption of hydrazine on the rhodium surface. If this is so then the adsorbed nitrogen-containing radicals produce ammonia by reaction with a further hydrazine molecule, the two nitrogen atoms of which form the nitrogen molecule.

The variation of rate of decomposition of hydrazine on the supported rhodium catalyst with respect to hydrazine concentration is shown in Fig. 2.

The rate of a reaction and the concentration of reactant may be related by

$$R = kc^n$$

where R is the rate, k is a rate constant, c is the concentration and n is the order of reaction. Writing this equation in the form

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

we may plot the data of Fig. 2 in the form \log_{10} rate with respect to \log_{10} hydrazine concentration as in Fig. 4. This plot shows that at concentrations up to 20% w/w hydrazine the rate of decomposition is almost proportional to the square root of the concentration, the value of n being 0.56. Over the range 20-50% w/w the value of n falls, becoming zero for concentrations of hydrazine above 50% w/w. The relationship of rate of reaction to concentration as shown in Fig. 2 is commonly found in heterogeneous catalysis when the rate controlling step of the reaction is an adsorption process and the kinetics may be explained by the use of the Langmuir adsorption isotherm. As the rate is proportional to the square root of the concentration in the low concentration range this indicates that the adsorption may be occurring with dissociation⁸ to cover two surface sites and this must be taken into account in applying the Langmuir adsorption isotherm.

A brief derivation of the Langmuir adsorption isotherm is as follows. If θ is the fraction of surface which is covered, then $(1-\theta)$ is the fraction which is bare, p is the pressure, or concentration, of the adsorbing species and k_1 and k_{-1} are the rate constants for adsorption and desorption respectively. Then for adsorption with dissociation to cover two surface sites, the rate of adsorption is

$$v_1 = k_1 p (1 - \theta)^2 .$$

Desorption involves two adsorbed species and the rate is

$$v_{-1} = k_{-1} \theta^2 .$$

At equilibrium the rates are equal, so that

$$k_1 p (1 - \theta)^2 = k_{-1} \theta^2 ,$$

$$\frac{\theta}{1 - \theta} = \left(\frac{k_1}{k_{-1}} p \right)^{\frac{1}{2}} = K^{\frac{1}{2}} p^{\frac{1}{2}} ,$$

and

$$\theta = \frac{K^{\frac{1}{2}} p^{\frac{1}{2}}}{1 + K^{\frac{1}{2}} p^{\frac{1}{2}}} .$$

The rate R of a heterogeneous reaction is proportional to the fraction of the surface which is covered, i.e.

$$R = k_2 \theta = \frac{k_2 K^{\frac{1}{2}} p^{\frac{1}{2}}}{1 + K^{\frac{1}{2}} p^{\frac{1}{2}}}$$

where k_2 is the rate constant of the decomposition reaction. Now

(a) at low concentrations p is small and $K^{\frac{1}{2}} p^{\frac{1}{2}} \ll 1$, so

$$R \approx k_2 K^{\frac{1}{2}} p^{\frac{1}{2}} ,$$

the rate of reaction being proportional to the square root of the concentration of the reactant (Fig. 4);

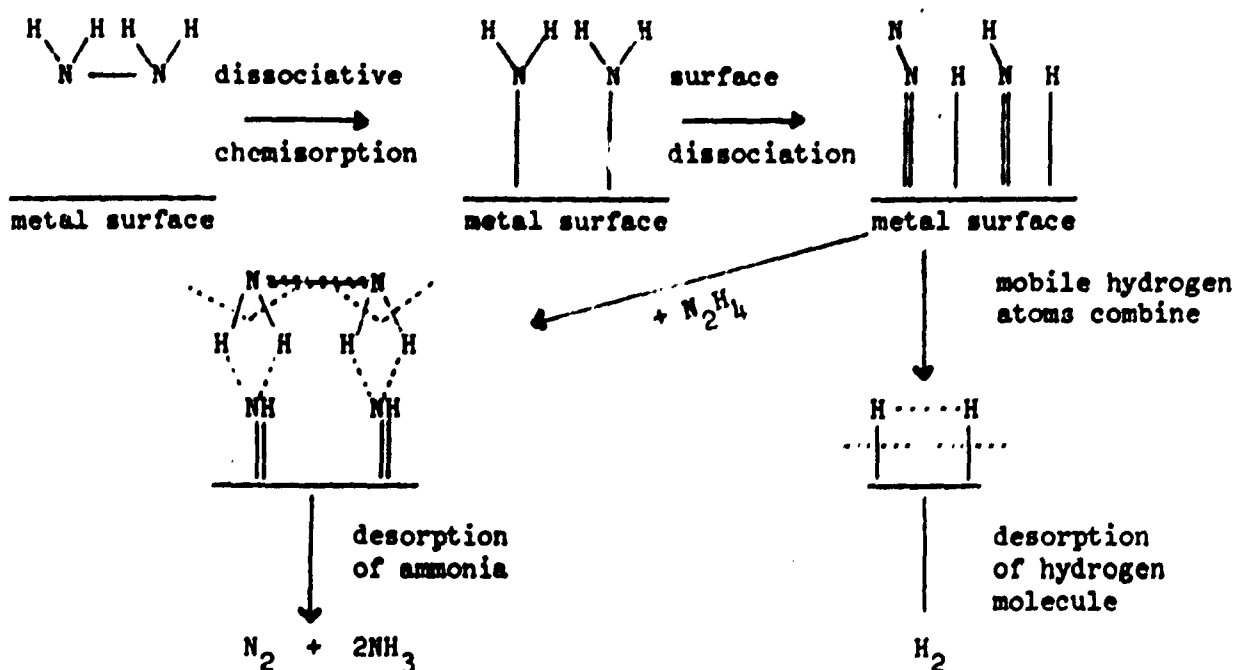
(b) at high concentrations p is large and $K^{\frac{1}{2}} p^{\frac{1}{2}} \gg 1$, so

$$R \approx k_2$$

and the rate of reaction is independent of the concentration of the reactant (Fig. 4).

At intermediate concentrations the rate of reaction is proportional to the concentration of the reactant to some power between $\frac{1}{2}$ and zero.

The observed kinetics of the decomposition of liquid hydrazine on a supported rhodium catalyst may therefore be explained by assuming that the dissociative chemisorption of hydrazine is the initial step and applying this to the Langmuir adsorption isotherm to derive the rate equations. As the overall reaction involves two hydrazine molecules and the nitrogen produced by the reaction is formed from the two nitrogen atoms of one hydrazine molecule² the reaction must occur between one dissociatively chemisorbed hydrazine molecule and one liquid phase or physically adsorbed hydrazine molecule, this being a Langmuir-Rideal reaction⁹. The initial step in the reaction is the chemisorption of hydrazine to form two NH_2 radicals adsorbed on two surface sites. Rhodium is not able to chemisorb nitrogen as atoms because there are insufficient d orbital vacancies to form the nitrogen-metal triple bond. However rhodium has one d electron more than ruthenium, which is capable of forming a triple bond to chemisorb nitrogen as atoms, and therefore it is to be expected that rhodium will have sufficient d orbital vacancies to form a double bond to chemisorb an NH radical. Therefore the second step in the reaction is postulated to be the surface dissociation of the NH_2 radical to NH and H . The adsorbed hydrogen atoms are mobile and combine to form the hydrogen molecule which is desorbed. Reaction then occurs between two adsorbed NH radicals and one hydrazine molecule, the NH radicals forming ammonia and the two nitrogen atoms of the hydrazine molecule forming nitrogen without nitrogen-nitrogen bond fission. The reaction mechanism may be represented as follows:-



If the temperature dependence of the rate of reaction is measured for hydrazine solutions of less than 50% w/w the activation energy calculated from the Arrhenius equation will only be an apparent activation energy as the rate equation contains two temperature dependent rate constants, k_2 and K . Therefore to determine the true activation energy of the decomposition reaction solutions of more than 50% w/w hydrazine must be used, and Fig. 3 shows an Arrhenius plot for the temperature of the rate of decomposition of 72.7% w/w hydrazine solution. The activation energy was calculated to be $41,300 \pm 340$ J mole⁻¹ ($9,876 \pm 81$ cal mole⁻¹) and the pre-exponential factor is 3.45×10^2 mole gm⁻¹ sec⁻¹.

5 CONCLUSIONS

Over the range of concentration, 0-20% w/w, the rate of decomposition of hydrazine, using a supported rhodium catalyst, is proportional to the square root of the concentration. At concentrations between 20-50% w/w the order of the reaction diminishes and for concentrations above 50% w/w it is zero. The activation energy for the reaction, calculated from the temperature variation of the rate of decomposition of 72.7% w/w hydrazine, is $41,300 \pm 340$ J mole⁻¹ (9876 ± 81 cal mole⁻¹) and the pre-exponential factor is 3.45×10^2 mole gm⁻¹ sec⁻¹.

The kinetics may be explained using the Langmuir adsorption isotherm to derive the rate equations on the assumption that the dissociative chemisorption of hydrazine to NH_2 radicals is the initial step in the reaction mechanism. The two NH_2 radicals further dissociate to form adsorbed NH and H atoms. The latter then combine and are desorbed as a hydrogen molecule. The NH radicals react with a physically adsorbed hydrazine molecule to form nitrogen and ammonia, the nitrogen molecule being formed from the two nitrogen atoms of the physically adsorbed hydrazine molecule without nitrogen-nitrogen bond fission.

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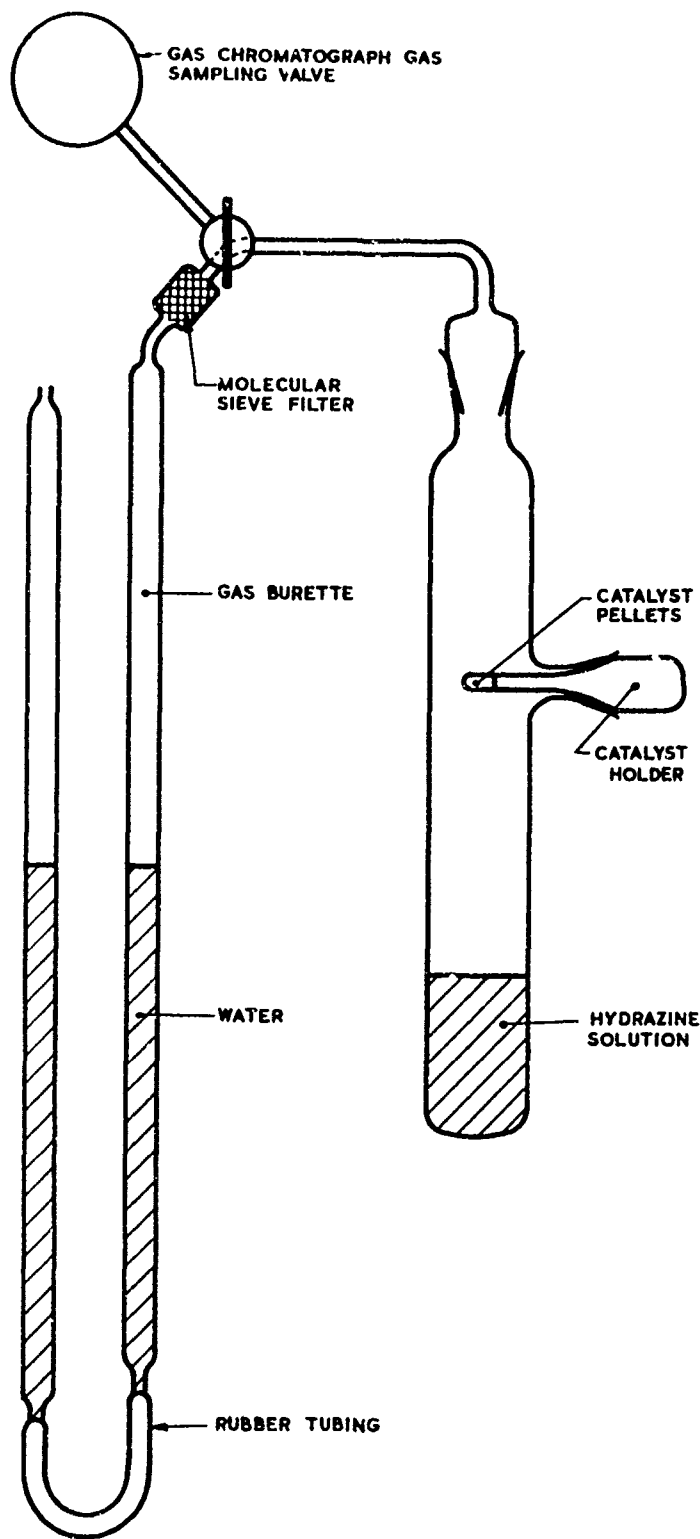


FIG. 1 APPARATUS USED TO MEASURE THE RATE OF DECOMPOSITION OF HYDRAZINE ON SUPPORTED RHODIUM CATALYST

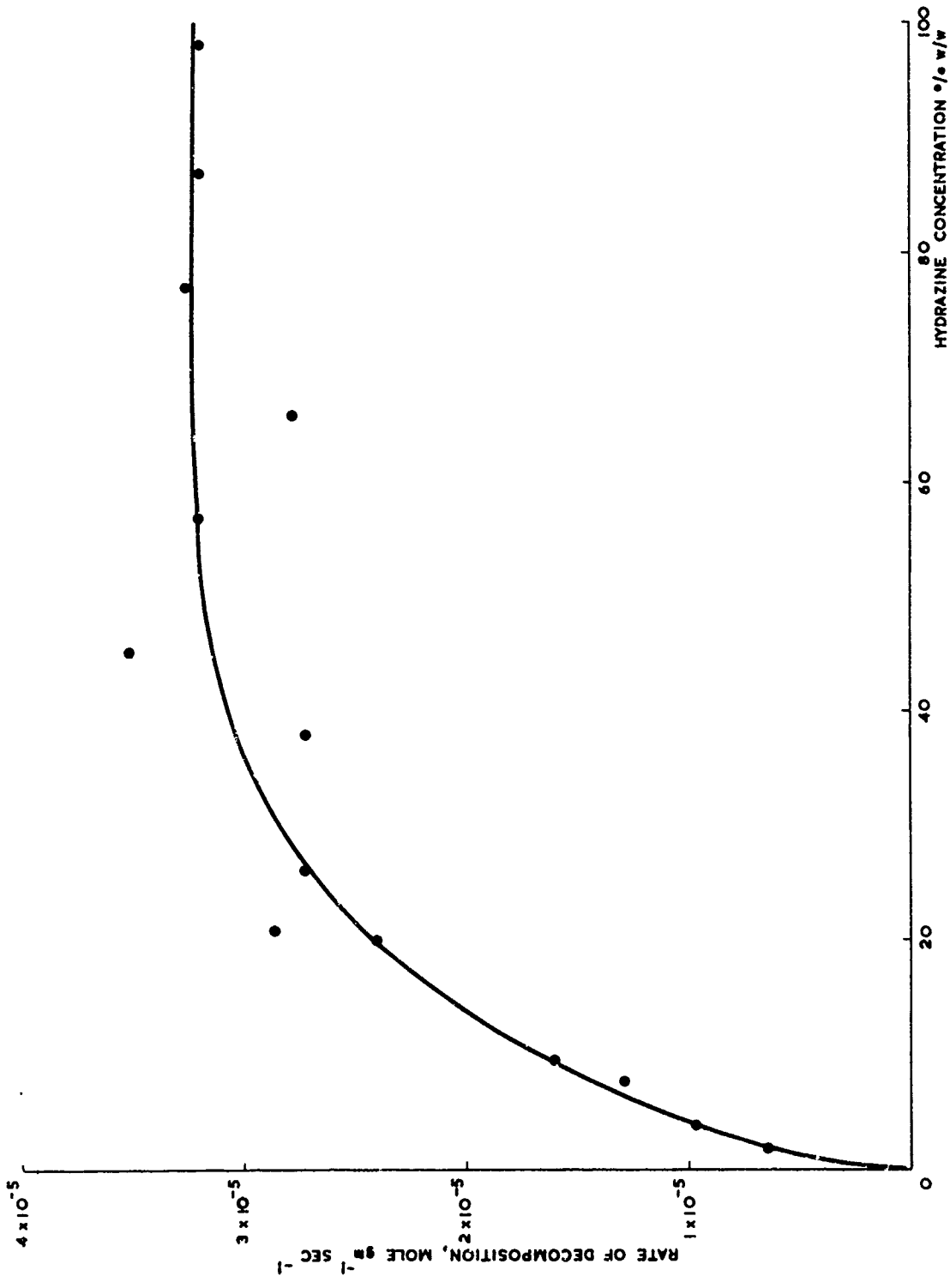


FIG. 2 RATE OF DECOMPOSITION OF HYDRAZINE ON 20% RHODIUM CATALYST
AT 21°C WITH RESPECT TO HYDRAZINE CONCENTRATION

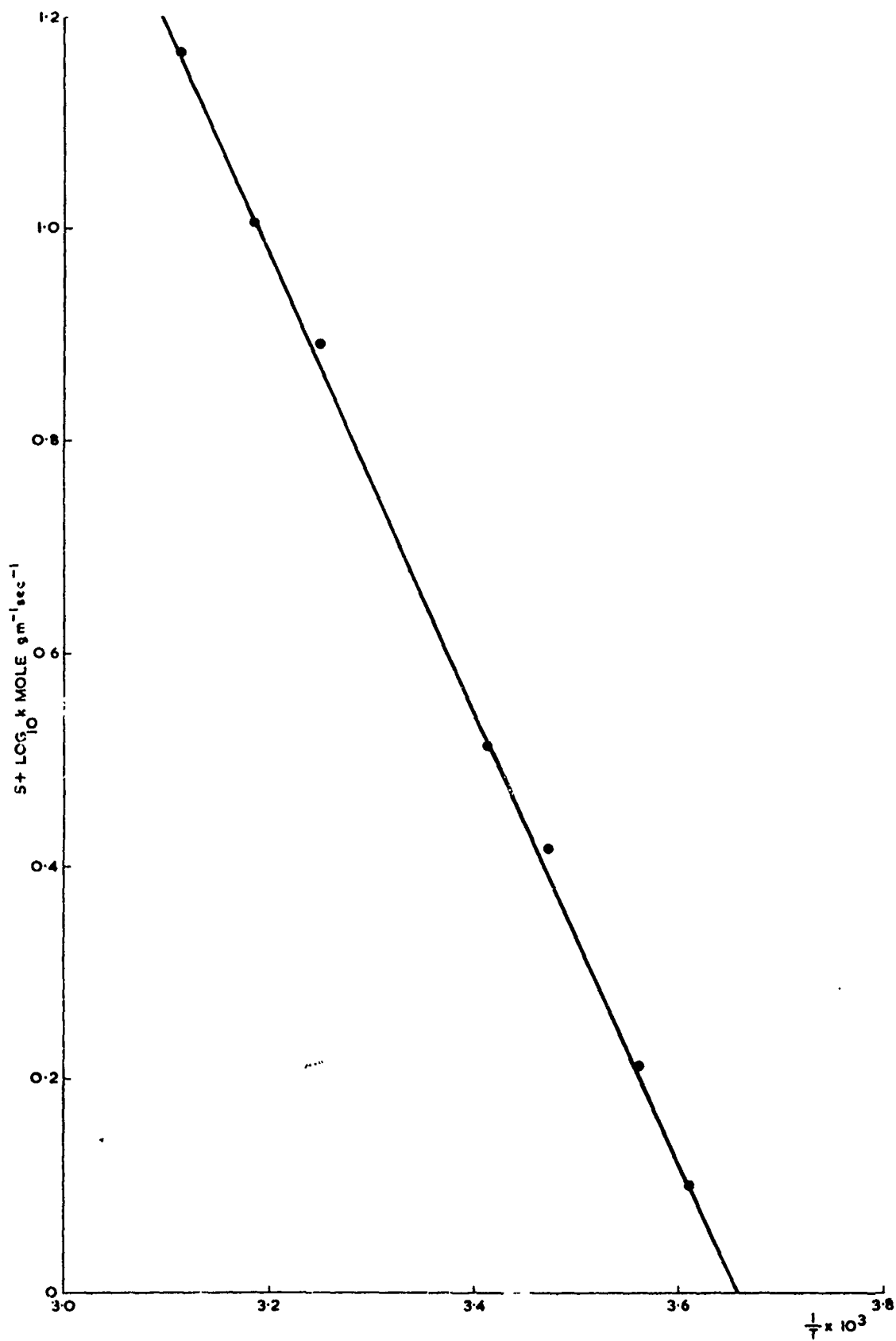


FIG. 3 ARRHENIUS PLOT FOR THE DECOMPOSITION OF 72.7% w/w
HYDRAZINE ON A SUPPORTED RHODIUM CATALYST

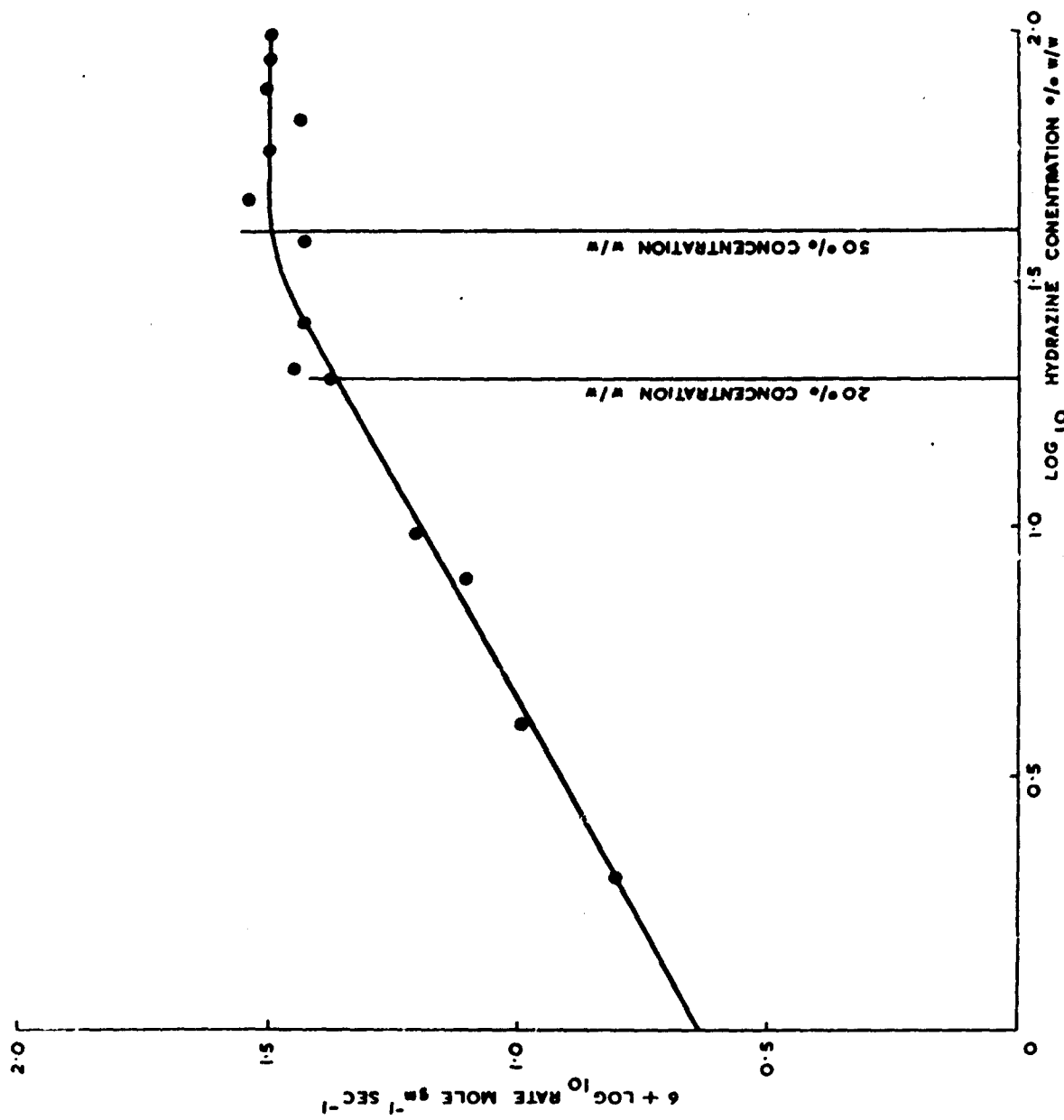


FIG. 4 PLOT OF \log_{10} RATE WITH RESPECT TO \log_{10} HYDRAZINE CONCENTRATION FOR THE DECOMPOSITION OF HYDRAZINE ON THE SUPPORTED RHODIUM CATALYST AT 21°C