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Very Low-Pressure Pyrolysis (VLPP) of Hydrazine, Ethanol, and Formic Acid on Fused Silica[1]

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The heterogeneous decomposition kinetics of N_2H_4 into N_2, NH_3, and H_2 have been investigated in a heat-treated fused-silica Knudsen cell flow reactor operating at pressures $\sim 10^{-6}$–10^{-3} Torr and temperatures of 600 to 1300 K. At temperatures above 1050 K, decomposition is best described by a rate half-order in N_2H_4 concentration with an activation energy of 37 kcal mole^{-1}. The H_2/N_2 ratio increases with temperature. NH_2 radicals were carefully looked for but not detected, indicating that they constituted <0.05 of the products even at 1300 K. At lower temperatures a relatively irreproducible reaction produces only N_2 and NH_3 products with activation energy of ~ 12 kcal mole^{-1}. The heterogeneous dehydration of C_2H_5OH and of HCOOH were briefly studied under very low-pressure conditions at temperatures above 1000 K and were found to generally obey half-order kinetics.

Results for all high temperature reactions are concordant with a mechanism involving a fast heterolytic adsorption followed by a unimolecular rate-limiting surface process.

I. INTRODUCTION

Reactions of gases on silica surfaces have been of interest in the study of catalytic processes and in overall gas reactions in silica vessels. The function and kinetics of silica catalysts, especially when combined with alumina, are of great interest in view of the industrial importance of these selective catalysts (*1*). On the other hand, as a result of the relative inert nature of the silica surface, fused-silica reactors are widely used in the study of gas reactions. However, in many cases, such surfaces are known to profoundly influence the chemical course of reaction; more detailed information concerning such reactions is required for the experimental interpretation of these systems.

The first quantitative data for N_2H_4 decomposition on silica were obtained by Askey (*2*) by static reactor pressure-rise experiments. The reaction was observed to be roughly first order over the temperature range 558–583 K and pressure range 20–150 Torr (1 Torr = 133.3 N m^{-2}), to have an activation energy of roughly 7 kcal mole^{-1} (1 kcal = 4.184 kJ), and to follow the stoichiometry of reaction [1]:

$$3N_2H_4 \rightarrow 4NH_3 + N_2. \qquad [1]$$

A small amount of H_2 was also noted as a product.

Szwarc (*3*) subsequently examined the reaction in a flow system containing several Torr of hydrazine at 874–1060 K and found the activation energy of reaction [1], $E_1 \sim 10$ kcal mole^{-1}, and the activation

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TABLE 1

Reactor Parameters[a]

Aperture diameter (cm)	10.3	3.10	0.81
Escape rate constant (sec^{-1})	20.8 $(T/M)^{1/2}$	2.13 $(T/M)^{1/2}$	0.143 $(T/M)^{1/2}$
Collision number	176	1930	29,000

[a] Volume, $V = 130\ \text{cm}^3$; surface area (assumed smooth), $A_w = 141\ \text{cm}^2$; collision frequency, $\omega = 4.15 \times 10^3\ (T/M)^{1/2}\ \text{sec}^{-1}$.

energy of reaction [2]:

$$2N_2H_4 \rightarrow 2NH_3 + N_2 + H_2, \qquad [2]$$

$E_2 \sim 20$ kcal mole^{-1}.

Hanratty *et al.* [4] examined the reaction in a silica vessel with argon carrier gas between 543–910 K at hydrazine pressures near 30 Torr. Activation energies of 15.3 kcal mole^{-1} and 9.3 kcal mole^{-1} for unpacked and packed reactor, respectively, were derived, and a small amount of H_2 was observed as a product.

Kant and McMahon (*5*) subsequently found, through isotopic-labeling studies in a Pyrex vessel at 543–598 K and 10–12 Torr, that N_2 product was formed from a single N_2H_4 molecule and thereby supported a complex concerted mechanism proposed by Szwarc (*3*).

The dehydration of C_2H_5OH and HCOOH on silica and silica–alumina surfaces have been studied by a number of investigators, although generally at higher pressure and lower temperature than in the present work. Results of Crocker and Robinson (*6*) for decomposition of HCOOH, however, were carried out 10^{-2}–10^{-3} Torr at 450–600 K, and the reaction probability, P, was reported as first order with a 19 kcal mole^{-1} activation energy.

In view of our capability to monitor pyrolysis in a fused-silica reactor (*7*) under conditions hitherto unexplored for such heterogeneous processes and because of the considerable interest in reactions on silica surfaces, we have carried out studies of the decomposition of hydrazine, along with less complete studies of C_2H_5OH and HCOOH, at very low pressures (10^{-7}–10^{-3} Torr) and high temperatures (600–1300 K).

II. EXPERIMENTAL DETAILS

The general theory and practice of very low-pressure pyrolysis experiments have been reviewed elsewhere (*7*). Briefly, a calibrated flow of hydrazine, generally with a comparable flow of argon, is passed through a temperature-controlled fused silica reaction cell. The flow is always kept low enough so that molecular flow conditions prevail in the reactor, resulting in well-stirred reaction conditions. Thus, the average number of collisions that a hydrazine molecule experiences with the wall before escaping through the exit aperture is dependent only on reactor geometry.

The flux from the reactor is analyzed by a quadrupole mass spectrometer. For the bulk of the studies, a detection chamber was used in which the partial pressures of reactants were sampled in a detection volume downstream of the reactor. In conjunction with this system, a triple exit aperture reactor was employed in which the residence time and the pressure within the reaction could be varied by changing the effective aperture through a manipulator outside of the reactor. Details of reactor geometry are given in Table 1.

For studies where NH_2 radical was searched for, a different detection system was used in which the flux from the reactor was first formed into a beam, then modulated by a mechanical chopper, and then detected via phase-sensitive detection. This insured that any species escaping from the reactor would be detected before collision outside of the reactor. A different fused-silica single aperture reactor (collision number ~300 collisions molecule^{-1}) was used for these studies.

The triple-aperture reactor was heat-treated *in vacuo* at 1300 K for several hours before any hydrazine runs and at several times in between experiments. This treatment was found to have no noticeable effect when carried out between experiments if the reactor was cooled to room temperature after such treatment.

The gas inlet system was fitted with silicone-lubricated stopcocks, and the detection chamber pumped with a refrigeration-baffled silicone oil diffusion pump. It is expected that the walls were continually exposed to these silicone vapors, and at higher temperatures the surface may have been coated with silicon oxides from their decomposition. While we believe that the heterogeneous decomposition reactions reported in this study occurred on silicon oxide surfaces, we cannot determine whether the behavior would be different for "clean" fused silica (which may, in any event, contain elements other than silicon and oxygen).

Reliable experimental measurements turned out to be more difficult to obtain than anticipated because of sorption of N_2H_4 on the walls of the Pyrex inlet system, the quartz reactor, and the stainless steel detection chamber. This caused "memory" effects that perturbed the measurements as the N_2H_4 flow changed (by reaction or by change in total flow). It was found that the time to reach steady-state flow decreased almost linearly with increasing flow rate. For example, when the temperature changed so that the fraction of unreacted N_2H_4 changed from 1.0 to 0.5, the time to reach steady-state conditions was ~5 min at a flow of 2×10^{16} molecules sec^{-1} and increased to ~50 min at a flow of 2×10^{15} molecules sec^{-1}.

Data presented in this paper were obtained in experiments designed to bypass this source of error. In each run the hydrazine flow rate and aperture were held constant and the temperature was slowly varied. Steady-state conditions were verified by holding the temperature constant for extended periods of time (1 hr was typical). Reaction rates were measured by monitoring the disappearance of the N_2H_4 mass spectral peak relative to the premixed argon peak, since the usual method of finding fractional decomposition from the peak height ratio of reactant flowing from the reactor to reactant flowing through a reactor-bypass valve proved unreliable because of adsorption effects in the inlet region.

At all but the highest flow rates, analysis of N_2 product was severely complicated by the presence of CO in the stainless steel detection chamber. Also, at these lower flows, product NH_3 analysis was impossible due to its affinity for metal surfaces. Consequently, in this flow regime ($<10^{16}$ molecules sec^{-1}), reliable values for product concentration could not be obtained. However, at higher flows, the reaction produced quantities of NH_3 and N_2 as products fairly consistent with the amount of N_2H_4 decomposed in accord with the reaction [1]. Small amounts of H_2 were observed at the highest temperatures.

Anhydrous hydrazine used for these experiments was from Olin–Matheson and found to contain $<2\%$ water and $<1\%$ of any other impurities detectable by mass spectrometry. Reagent grade ethanol and 40% formic acid in water were used for their respective pyrolyses. Additional water was added to the reactant mixture for each of these three reactions to test for any effect on the decomposition rates. No effect was observed in any case.

For all reactions, overall rates were derived from measurements of the disappearance of the parent mass spectral peak corresponding to the reactant molecule.

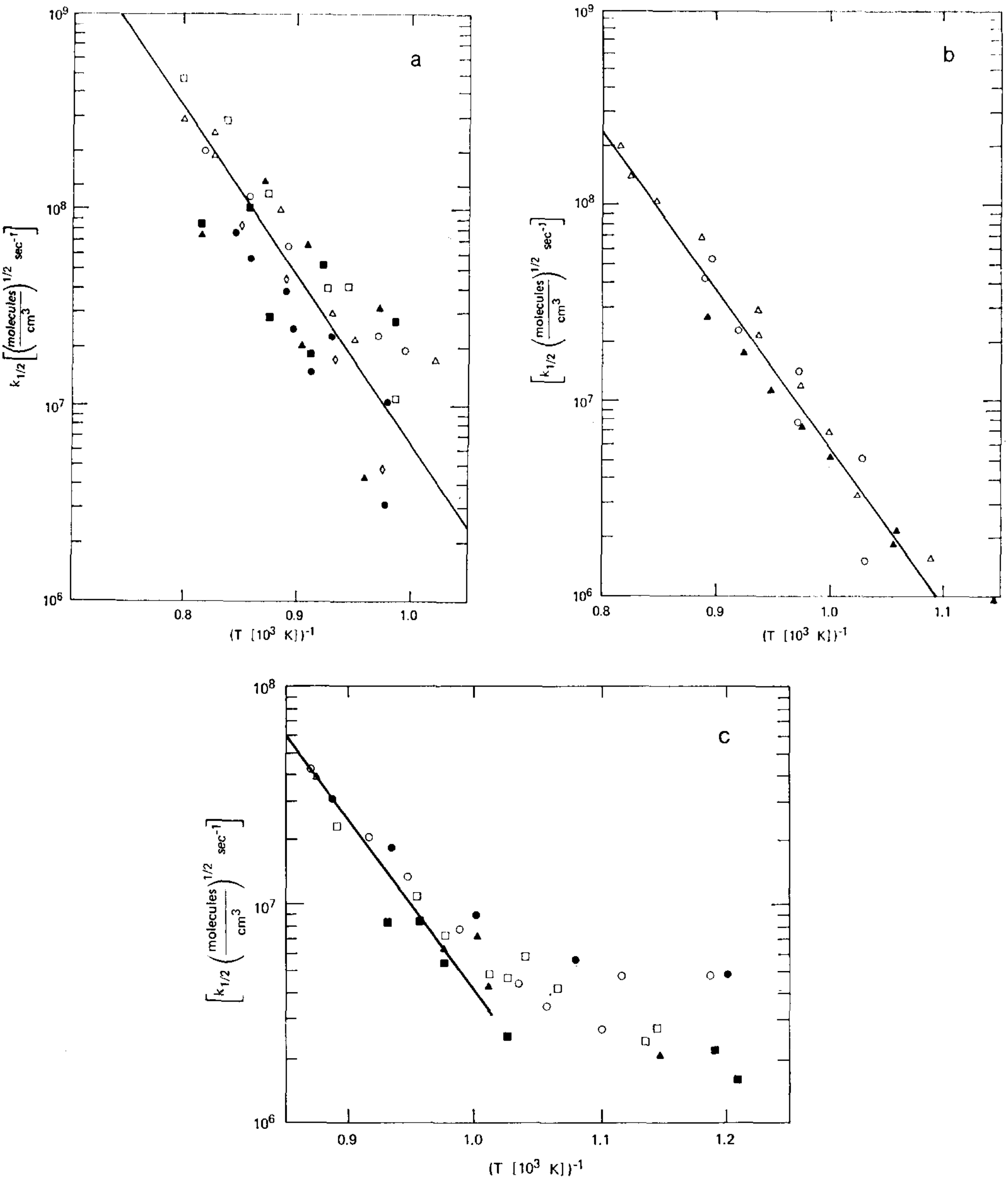

FIG. 1. Arrhenius plots for decomposition of hydrazine in a quartz, triple-aperture, VLPP reactor. (a) Measurements with 176 collisions molecule^{-1} reactor: Flow (10^{15} molecules sec^{-1}) □, 20; △, 16; ○, 11; ◇, 7.7; ■, 1.9; ♦, 1.8; ▲, 1.4. (b) Measurements with 1930 collisions molecule^{-1} reactor: Flow (10^{15} molecules sec^{-1}) △, 18; ○, 8.8; ▲, 1.9. (c) Measurements with 2.9×10^3 collisions molecule^{-1} reactor: Flow (10^{15} molecules sec^{-1}) ●, 15; ○, 4.6; □, 2.1; ▲, 1.5; ■, 1.4.

III. RESULTS

All analyses implicitly assume no surface roughness. This amounts to not considering collisions occurring "within" the surface (i.e., only initial collisions with surface are counted). Also, any change in effective surface area with temperature would be manifested as a change in the reported rate constant. In the above sense, our measured rates may be regarded as global.

Low-Temperature Hydrazine Decomposition (575–900 K)

In the small aperture reactor (~29,000 collisions molecule^{-1}), decomposition of N_2H_4 into N_2 and NH_3 was clearly observed in the above temperature range. No H_2 was seen as a product. Extent of reaction was somewhat dependent on the recent history of the reactor and reached a minimum of 50–60% in the range 650–800 K. The reproducibility of this reaction was poor, but if first-rate behavior is assumed, an activation energy of 10–14 kcal mol^{-1} characterizes the temperature dependence around 500 K.

High-Temperature Hydrazine Decomposition (875–1275 K)

At these higher temperatures, the decomposition of N_2H_4 could be investigated using all three apertures (roughly 1-, 3-, and 10-mm in diameter) of the VLPP reactor. The results were analyzed on the basis of a half-order reaction. Using the relationship:

$$R_A = k_e[A] + k_{\frac{1}{2}}[A]^{\frac{1}{2}} = k_e[A]_0,$$

the half-order rate constant is:

$$k_{\frac{1}{2}} = (k_e f_r R_A)^{\frac{1}{2}} \frac{(1 - f_r)}{f_r},$$

where the terms are defined as: R_A = flow of N_2H_4 into reactor per unit reactor volume (molecules cm^{-3} sec^{-1}), $k_e \equiv$ reactor escape rate constant (sec^{-1}), $[A] \equiv$ steady-state concentration of N_2H_4 (molecules cm^{-3}), $[A]_0 \equiv$ steady-state concentration of N_2H_4 at $k_{\frac{1}{2}} = 0$, and f_r = fraction of N_2H_4 remaining $[A]/[A]_0$.

The variations of $k_{\frac{1}{2}}$ with temperature in terms of Arrhenius plots are displayed in Fig. 1a–c for three different apertures, and the kinetic parameters derived from them are given in Table 2. Figure 2 shows $k_{\frac{1}{2}}$ versus flow rate at the representative temperature of 1025 K. Noteworthy points concerning this reaction are:

TABLE 2

Arrhenius Parameters for Hydrazine Decomposition on Fused Silica

Aperture diameter (mm)	A-factor (10^{-14} molecules$^{\frac{1}{2}}$ cm$^{-\frac{3}{2}}$ sec^{-1})	Activation energy (kcal mole^{-1})
10	13 ± 6	38.1 ± 1.0
3	7.4 ± 2.0	37.1 ± 1.0
1	3.0 ± 1.5	36.0 ± 3.0

(i) The leveling-off of the rate for the smallest aperture at lower temperatures (Fig. 1c) is due to the lower-temperature reaction discussed previously.

(ii) The apparently low Arrhenius parameters for the 1-mm aperture (Table 2), as well as the larger uncertainty of the measurement in this case, may result from uncertainty due to the smaller temperature range over which these data were obtained.

(iii) In Fig. 2, note that within experimental uncertainty, rates for the 1- and 3-mm aperture reactor are coincident and generally flow-independent. However, flow-dependent behavior apparently begins to occur for decomposition in the 10-mm aperture reactor experiments. At the lower flows in this reactor, first-order kinetics may be approached.

(iv) At temperature >1200 K, the rate was found to decrease with time. This behavior was reproducible and amounted to a factor of ~2–3 in $k_{\frac{1}{2}}$ over ~1 hr. By cooling and reheating, the behavior could be reproduced. This is apparently due to a slow reversible deactivation of silica in this temperature region.

(v) No effect of added H_2O, NH_3, N_2, or H_2 on the rate was found.

(vi) Quantitative analysis of the H_2 product was not attempted. However, the peak associated with H_2 was not observed below 1100 K and was found to increase relative to the argon carrier peak above this temperature. We estimate that for the

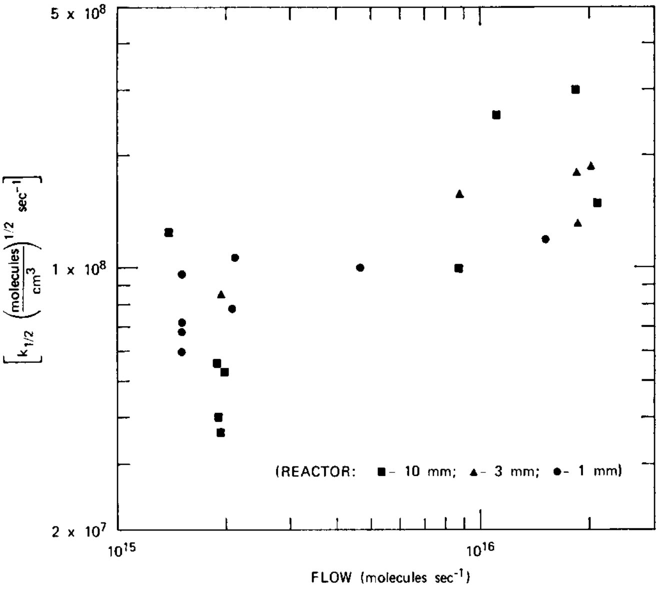

FIG. 2. Plot of half-order rate constants as a function of flow for three aperture sizes at 1025 K for the decomposition of N_2H_4 on fused silica.

majority of the runs, the relative amount of H_2 to NH_3 was $\lesssim 0.15$.

(vii) Separate experiments were performed to search for NH_2 radical products. A reactor with collision number similar to that of the 10-mm aperture reactor was used in conjunction with a modulated-beam mass spectrometric detection system. No NH_2 radicals were seen using low-electron energy (<25 eV) relative to the NH_3 product. We estimate from these studies that $[NH_2]/[NH_3] < 0.05$.

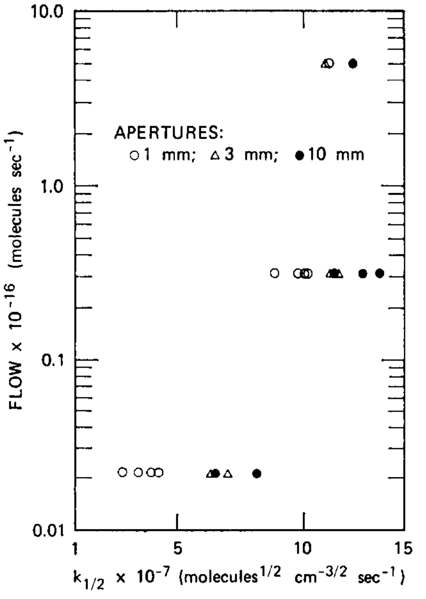

FIG. 3. Variation of $k_{\frac{1}{2}}$ with flow for ethanol dehydration on fused silica.

Dehydration of C_2H_5OH and HCOOH on Fused Silica

A brief study was made of the heterogeneous dehydration of ethanol to ethylene and water at 1173 K. Dehydrogenation was found to be a minor ($\leq 5\%$) competing process of higher activation energy. Since for this molecule (and for formic acid, as well) adsorption problems were minimal, the study could be carried out over a wide range of flow rates from 2.2×10^{14} to 5×10^{16} molecules sec^{-1} (see Fig. 3). Since three apertures were used to vary the pressure by a factor of ~ 150 under a given flow, an overall pressure range of $\sim 10^{-3}$ to 10^{-7} Torr was obtained. Half-order kinetics again were used to analyze the results because it was found to be the best single

TABLE 3

Half-Order Rate Constants Derived from the Dehydration of Formic Acid on Fused Silica at 1073 K

Flow rate (10^{16} molecules $\sec^{-1}$)	Aperture (mm)	Fraction H_2CO_2 remaining	$k_{\frac{1}{2}}$ (10^8 molecules$^{\frac{1}{2}}$ cm$^{-\frac{1}{2}}$ $\sec^{-1}$)	First-order rate constant ($\sec^{-1}$)
5.0	10	0.92	1.89	8.85
5.0	3	0.79	1.72	2.78
5.0	1	0.45	1.55	0.863
0.33	10	0.85	0.90	19.7
0.33	3	0.56	1.09	8.17
0.33	1	0.34	0.55	1.36
0.022	10	0.60	0.63	52.2
0.022	3	0.33	0.52	20.6
0.022	1	0.13	0.39	4.51

order correlating data over the range of experimentation. The agreement with such kinetics is not perfect, as seen in Fig. 3 (e.g., the larger aperture reactor yields consistently larger rates). At lower flows, the kinetics also begin to deviate from half-order kinetics; however, even in this range, it describes the kinetics far better than a first-order model.

Some runs were also carried out on the dehydration of formic acid to carbon dioxide and water in the same quartz reactor at 1073 K. As seen in Table 3, half-order kinetics correlated all of the data much better than first-order kinetics. Note that over a 5×10^4 range of pressure, $k_{\frac{1}{2}}$ varied only by a factor of ~ 4, while the first-order rate varied by a factor of ~ 60. Also, at any given flow, $k_{\frac{1}{2}}$ varied by $< 50\%$, while k_1 varied by a factor of 10–15. However, for both of these decomposition reactions, a reaction order of $\sim \frac{3}{4}$ would best describe the reaction for results with a constant collision number reactor under varying flows. However, such a reaction order would lead to even poorer overall agreement with the data.

IV. DISCUSSION

Low-Temperature Hydrazine Decomposition

If this reaction is presumed to be of first order, then the derived activation energy of 10–14 kcal mole^{-1} agrees well with those of Szwarc (*3*) of ~ 10 kcal mole^{-1} and Hanratty *et al.* (*4*) of 9.3–15.7. However, we cannot exclude the possibility of a fractional order reaction occurring in our experiments. The variability of the rate and the barely measurable amount of decomposition occurring in the 3-mm aperture reactor obscured the reaction order. This variability of rate has been noted by other workers (*2–4*).

High-Temperature Mechanism for Hydrazine Decomposition

Since it is clear that gas-phase radicals do not play a major part in N_2H_4 decomposition in a fused silica reactor (see later in this section), we must invoke a mechanism in which the intermediates involved in the reaction are absorbed on the surface. Following is such a general scheme:

$$N_2H_4(\text{gas}) \underset{k_d}{\overset{k_a}{\rightleftarrows}} N_2H_{3,s} + H_s \qquad [3]$$

$$N_2H_{3,s} \xrightarrow{k_1} NH_3(\text{gas}) + N_s \qquad [4]$$

$$N_s + H_s \xrightarrow{k_{\text{fast}}} \cdots \rightarrow \tfrac{1}{3}NH_3(\text{gas}) + \tfrac{1}{3}N_2(\text{gas}) \qquad [5]$$

in which $N_2H_{3,s}$, H_s, and N_s are bound surface species.

This mechanism will result in half-order kinetics under the following two conditions.

Condition I requires that step [3] occur under low surface coverage, and follows Langmuir adsorption–desorption kinetics. Stated more explicitly, this condition requires that the fraction of catalytic sites covered under steady-state conditions, θ, is small ($\overset{\sim}{<}0.3$) and the heats of adsorption on these sites are uniform. Although the very low pressure and high temperature conditions of our experiments might intuitively imply low surface coverage, and there is no reason to expect any other type of adsorption energy distribution, this assumption must ultimately rest on its ability to predict observed behavior.

Assuming condition I, then:

$$[\mathrm{NH_3}] = \frac{k_a[\mathrm{N_2H_4(gas)}]}{k_d[\mathrm{H}_s] + k_1}. \tag{1}$$

Condition II requires reaction [4] to be the rate-limiting step; this is expressed in inequalities (2) and (3):

$$k_1 \ll k_d[\mathrm{H}_s] \tag{2}$$

$$k_1 \ll k_{\mathrm{fast}}[\mathrm{H}_s]. \tag{3}$$

Steady-state conditions for $\mathrm{N_2H}_{3,s}$ and relation (2) lead to:

$$[\mathrm{N_2H}_{3,s}] = \frac{k_a[\mathrm{N_2H_4(gas)}]}{k_d[\mathrm{H}_s]}. \tag{4}$$

Relation (3) along with both the mass balance relation (Eq. 5),

$$[\mathrm{H}_s] = [\mathrm{N_2H}_{3,s}] + [\mathrm{N}_s], \tag{5}$$

and the steady-state expression for $[\mathrm{N}_s]$ results in $[\mathrm{H}_s] = [\mathrm{N_2H}_{3,s}]$. This result, combined with Eq. (4), results in the following half-order rate expression:

$$-\frac{d[\mathrm{N_2H_4(gas)}]}{dt} = k_1[\mathrm{N_2H}_{3,s}] = k_1\left(\frac{k_a}{k_d}[\mathrm{N_2H_4(gas)}]\right)^{\frac{1}{2}}. \tag{6}$$

If, at some very low $\mathrm{N_2H_4}$ pressure, inequality (2) is reversed, then Eq. (1) becomes:

$$\text{rate} = k_1[\mathrm{N_2H}_{3,s}] = k_a[\mathrm{N_2H_4(gas)}].$$

If inequality (3) is reversed:

$$\text{rate} = k_{\mathrm{fast}}[\mathrm{N}_s][\mathrm{H}_s] = \frac{k_{\mathrm{fast}}k_1}{k_d}k_a[\mathrm{N_2H_4(gas)}].$$

This model, therefore, predicts first-order kinetics at low enough hydrazine pressures.

Figure 3 shows the range of consistency of half-order kinetics. In the large aperture (low pressure) reactor, at a flow of $\sim 2 \times 10^{16}$ molecules sec^{-1}, first-order kinetics begins to describe the rate more consistently. Unfortunately the experimental scatter makes it impossible to pinpoint the midpoint of the transition from half-order kinetics to first-order kinetics.

It is conceivable, however, that the observed kinetics may result from rate-limiting adsorption of a non-Langmuir type, specifically one involving a distribution of binding site energies which result in the expression:

$$\theta \alpha [\mathrm{N_2H_4(gas)}]^{\frac{1}{2}}.$$

In this case, if the rate of reaction is simply proportional to θ, half-order kinetics would result. However, the above constant form of θ must hold over a wide range of pressures (10^{-2}–10^{-5} Torr), temperatures (900–1200 K), and reaction rates (two orders of magnitude) for this mechanism to be operative. For this reason we do not favor this mechanism, although our data do not permit us to rigorously exclude it.

We will now show that the observed half-order rates preclude the formation of substantial pressures of gas-phase $\mathrm{NH_2}$ species. If the walls bring about the gas-phase equilibrium,

$$\mathrm{N_2H_4} \underset{k_r}{\overset{k_f}{\rightleftarrows}} 2\mathrm{NH_2}, \tag*{[6]}$$

where both $\mathrm{N_2H_4}$ and $\mathrm{NH_2}$ are gas-phase species, then to achieve half-order kinetics we must assume the first-order rate limiting step (the left-most step of reaction sequence [7]),

$$NH_2 \xrightarrow{k_1'} \cdots \rightarrow \tfrac{2}{3}NH_3 + \tfrac{1}{6}N_2. \quad [7]$$

This step competes with first-order escape from the reactor

$$NH_2 \xrightarrow{k_e} \text{escape}. \quad [8]$$

In the steady-state

$$[NH_2] = \frac{2k_f[N_2H_4]}{2k_r[NH_2] - k_1' - k_e}.$$

If

$$2k_r[NH_2] \gg k_1' + k_e,$$

then

$$\text{rate} = k_1'[NH_2] = k_1'\left(\frac{k_f}{k_r}[N_2H_4]\right)^{\frac{1}{2}}.$$

Note also that the complete equilibration of step [6] is required for this mechanism to yield half-order kinetics, and it must be catalyzed by the walls. The homogeneous gas-phase bond scission of N_2H_4 leading to NH_2 radicals would be slow under our experimental conditions due to the large degree of "fall-off" for N_2H_4 in the pressure range of these experiments. The reverse recombination reaction must also, of course, be wall-catalyzed (the wall acting as a "third" body).

The equilibrium constant, $K_{eq} = k_f/k_r$, for reaction [6] may be computed from the available data (*6, 7*), as $K_{eq} = 10^{13.0\pm0.7}$, at 1100 K. Since $k_{\frac{1}{2}} = 10^{7.5\pm0.2}$ molecules$^{\frac{1}{2}}$ cm$^{-\frac{3}{2}}$ sec^{-1} at 1100 K, and $k_1' = k_{\frac{1}{2}}K_{eq}^{-\frac{1}{2}}$, then at 1100 K,

$$k_1' = 10^{1.0\pm0.6}\ \text{sec}^{-1}.$$

Since from steps [7] and [8],

$$\frac{[NH_2]}{[NH_3]} = \frac{3}{2}\frac{k_e}{k_1'}$$

and k_e for the 10-, 3-, and 1-mm apertures equals 122, 12.5, and 0.838 sec^{-1}, respectively, the above ratio yields 19.5, 2.0, and 0.13, respectively. Thus, it is clear that for this model to be valid, a substantial fraction of products in the large and medium aperture reactor would have to be NH_2 radicals. This would not be consistent with the observed half-order kinetics, nor with the observation that the $[NH_2]/[NH_3] < 0.05$. This model cannot be correct; NH_2 gas-phase radicals are not major species in this reaction.

HCOOH and C_2H_5OH Dehydration

These reactions follow kinetics similar to each other and to the N_2H_4 decomposition reaction. Therefore, we propose an analogous mechanism for the HCOOH reaction:

$$HCOOH(\text{gas}) \rightleftarrows HCOO_s + H_s$$

$$HCOO_s \rightarrow CO(\text{gas}) + OH_s \quad \text{(rate-limiting)}$$

$$H_s + OH_s \rightarrow H_2O(\text{gas}).$$

An equivalent mechanism can also be written for the C_2H_5OH dehydration.

V. CONCLUSIONS

We have shown that the high temperature, low-pressure decomposition kinetics of N_2H_4, C_2H_5OH, and HCOOH on fused silica generally follow half-order kinetics and, at least in the case of the N_2H_4 reaction, gas-phase radicals play no important part in the reaction. Since we have found that the $N_2H_4 \rightleftarrows 2NH_2$ gaseous equilibrium is not achieved, we do not expect surface-bound NH_2 radical intermediates to be of mechanistic importance. Therefore, decomposition mechanisms probably involve ionic or semi-ionic surface intermediates. We propose that the mechanism consists of a preequilibrium of gaseous N_2H_4, C_2H_5OH, and HCOOH with the surface-bound pairs $N_2H_3^-$–H^+, $C_2H_5O^-$–H^+, and $HCOO^-$–H^+, respectively, followed by a rate-limiting first-order reaction of the former member of each pair. Fast subsequent surface reactions ultimately yield observed molecular products.

At the very lowest pressures studied, the kinetics rise from half-order toward first-order, indicating that under these conditions the initial heterolytic adsorption step or a step after the unimolecular process becomes rate limiting. A relatively small, but measurable, decrease in the calculated half-order rate constant with decreasing flow for constant collision number reactors remains unexplained by this model.

We cannot, however, exclude the possibility that the observed kinetics can be explained by an appropriate distribution of binding side energies.

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