INVESTIGATION OF N_2H_4 AND H_2O_2 DECOMPOSITION IN LOW AND HIGH PRESSURE SHOCK WAVES

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The thermal dissociation of H_2O_2 and N_2H_4, highly diluted with argon, has been investigated in shock waves. For N_2H_4 the complete fall-off curve from the low pressure to the high pressure region could be studied. Experiments at about $[Ar] = 3 \times 10^{-6}$ mole/cm³ yielded a limiting low pressure rate constant of $k_{1\,0} = 10^{15.6} \exp{[-(41 \text{ kcal/mole})/RT]}$ [cm³/mole sec] at $1280° \leq T \leq 1580°K$; experiments at about $[Ar] = 2 \times 10^{-3}$ mole/cm³ yielded a limiting high pressure rate constant of $k_{1\,\infty} = 10^{13.9} \exp{[-(55 \text{ kcal/mole})/RT]}$ [sec⁻¹] at $1110° \leq T \leq 1400°K$.

The unimolecular dissociation of H_2O_2 near the low pressure limit was investigated by an ultraviolet absorption technique, which gave $k_{4\,0} = 10^{16.5} \exp{[-(43 \text{ kcal/mole})/RT]}$ [cm³/mole sec] between $950°$ and $1450°K$. Experiments at 20 atm indicated the beginning of the fall-off region. In addition to H_2O_2, light absorption, corresponding to a species which forms and is consumed again during the reaction, was observed around 2300 Å. The origin of this absorption, possibly due to HO_2, is discussed.

For both decomposition reactions, the role of the corresponding consecutive reactions has been investigated. The rate constants of the unimolecular reactions are interpreted in terms of theories of unimolecular reactions and are compared. Nonequilibrium theories are applied to the low pressure constants; different activated complexes are considered for the high pressure constants.

Introduction

The thermal decomposition of N_2H_4 and H_2O_2 can be studied under conditions such that only unimolecular dissociation or at most a simple nonchain reaction occurs. Both decomposition reactions show a number of similarities.

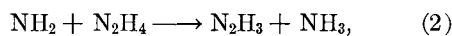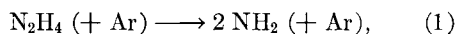The unimolecular reactions occur via the breaking of the corresponding bonds

$$HO\text{-}OH \rightarrow 2\,OH,$$

$$H_2N\text{-}NH_2 \rightarrow 2\,NH_2.$$
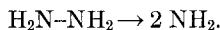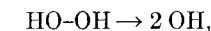
In addition, the first consecutive reactions discussed correspond to each other. The molecules are isoelectronic with bond energies that are similar $[D(HO\text{-}OH) \approx 49$ kcal/mole, $D(H_2N\text{-}NH_2) \approx 55$ kcal/mole$]$. Due to the related structures, one can expect similar "activated complexes" for unimolecular dissociation. Thus, a comparison of the high pressure limiting rates, which are determined mainly by the structure of the activated complexes, would be quite informative. On the other hand, the different numbers of oscillators should influence the low pressure limiting rates significantly.

In parts I and II of this paper, shock tube measurements of the thermal decomposition of N_2H_4 and H_2O_2 are described. The results are compared in terms of theories of unimolecular reactions in part III.

I. Decomposition of N_2H_4

Previous work on N_2H_4 decomposition is described by various authors.[1-5] In these studies difficulties arising from sensitivity to wall reactions and disturbances due to water impurities could be eliminated. However, there exists some doubt as to the role of consecutive reactions. Simple nonchain mechanisms of the type

$$N_2H_4 (+ \text{Ar}) \longrightarrow 2\,NH_2 (+ \text{Ar}), \qquad (1)$$

$$NH_2 + N_2H_4 \longrightarrow N_2H_3 + NH_3, \qquad (2)$$

$$NH_2 + N_2H_3 \longrightarrow NH_3 + N_2 + H_2, \qquad (3)$$

have been discussed.[3] With quasistationary concentrations of NH_2 and N_2H_3 they lead to:

$$d[N_2H_4]/dt = -2k_1[N_2H_4].$$

For sufficiently low temperatures and high N_2H_4 concentrations, there is also evidence for a chain mechanism. This can be concluded, among other things, from induction periods observed by Michel and Wagner[4] at $T \leq 1200°K$ and $[N_2H_4] \geq 10^{-7}$ mole/cm³. However, it does not seem to be clear yet, under what conditions chain reactions become important.[3–5] Additional difficulties in the interpretation of experimental results arise from the fact that the order of Reaction (1) changes markedly in the pressure range between 1 and 10 atm.

In order to give a complete and consistent picture of N_2H_4 decomposition it is necessary to know the rate of Reaction (1) accurately. This requires experiments at low N_2H_4 concentrations, to minimize difficulties from the mechanism. Further, the pressure must be varied over a large range to obtain the complete fall-off curve from which the limiting rates are determined.

Low Pressure Experiments

Experiments at low total gas pressures have been performed in incident shock waves. The dissociation of N_2H_4, diluted with argon, has been followed by the time history of N_2H_4 light absorption at 2300 Å. The 10 cm i.d. aluminum shock tube, the additional equipment and the experimental procedure have been described by Jost *et al.*[12] and Olschewski *et al.*[13]

The temperature range in this series of runs was $1280° \leq T \leq 1580°K$. Argon concentrations were between 2×10^{-6} and 3×10^{-5} mole/cm³ (corresponding to pressures between 0.2 and 4 atm). The relative N_2H_4 concentrations in Ar varied between 0.2% and 0.5%, giving absolute N_2H_4 concentrations from 4×10^{-9} at higher temperatures to 3×10^{-8} mole/cm³ at lower temperatures. The highest Ar concentrations overlapped with conditions used by Michel and Wagner[4] in reflected shock wave experiments. The good agreement of the results is shown in Fig. 3.

Under the conditions described, the N_2H_4 concentration followed first order rate laws. As low N_2H_4 concentrations and relatively high temperatures were used, no such induction periods and effects of the N_2H_4 concentration on the experimental rate constants as in Michel and Wagner's work were observed. In measurements in $[Ar]$ below 6×10^{-6} mole/cm³, the first order rate constants were found to be proportional to $[Ar]$, within the experimental accuracy. These experiments

$$2 \times 10^{-6} \leq [Ar] \leq 6 \times 10^{-6} \text{ mole/cm}^3,$$

$$1280° \leq T \leq 1580°K$$

are shown in Fig. 1. The rate constants k'_{10} of $d[N_2H_4]/dt = -k'_{10}[Ar][N_2H_4]$ can be described by

$$k'_{10} = 10^{15.6} \exp\{-[(41 \pm 2) \text{ kcal/mole}]/RT\}$$
$$\times [\text{cm}^3/\text{mole sec}].$$

High Pressure Experiments

Experiments at pressures up to 300 atm were carried out in reflected shock waves in a 7.5 cm i.d. high pressure shock tube made of steel. This shock tube has been described by Olschewski *et al.*[14] In several previous investigations, it was shown to give only small deviations from ideal shock wave behavior—e.g., small attenuations of the shock velocity. In calculating the high pressure shock wave data, one must take into account the pressure dependence of the Ar enthalpy and the deviations from the ideal gas law.[15] The temperature range of the high pressure experiments was $1050° \leq T \leq 1400°K$. The Ar concentrations varied between 2×10^{-4} and 3×10^{-3} mole/cm³ (corresponding $20 \leq p \leq 300$ atm). The N_2H_4 concentrations varied between 1.5×10^{-8} and 60×10^{-8} mole/cm³. The relative N_2H_4 concentrations were always less than 0.1%, sometimes down to $10^{-3}\%$ in Ar, avoiding complications due to the heat of reaction etc. in all cases.

As with the low pressure experiments at N_2H_4 concentrations $\leq 3 \times 10^{-8}$ mole/cm³, no N_2H_4 concentration effects on the first order rate constants were observed in the high pressure experiments with $1.5 \times 10^{-8} \leq [N_2H_4] \leq 5 \times 10^{-8}$ mole/cm³. In Fig. 2, at $[N_2H_4] > 10 \times 10^{-8}$ mole/cm³, an increase of the first order rate constants by about a factor of 2 is observed at lower temperatures. This increase is nearly the same between 10×10^{-8} mole/cm³ and 60×10^{-8} mole/cm³, for $T \simeq 1050°–1150°K$, and disappears at $T \approx 1400°K$. No induction periods were observed.

The experimental first order rate constants were found to be independent of the total pressure at $[Ar] \geq 10^{-3}$ mole/cm³ within the experimental accuracy. Experiments with

$$1.5 \times 10^{-8} \leq [N_2H_4] \leq 5 \times 10^{-8} \text{ mole/cm}^3$$

and

$$10^{-3} \leq [Ar] \leq 3 \times 10^{-3} \text{ mole/cm}^3$$

(see Fig. 2) give a first order rate constant $(1100° \leq T \leq 1400°K)$

$$k'_{1\infty} = 10^{13.7} \exp[-(54 \pm 2) \text{ kcal/mole})/RT]$$
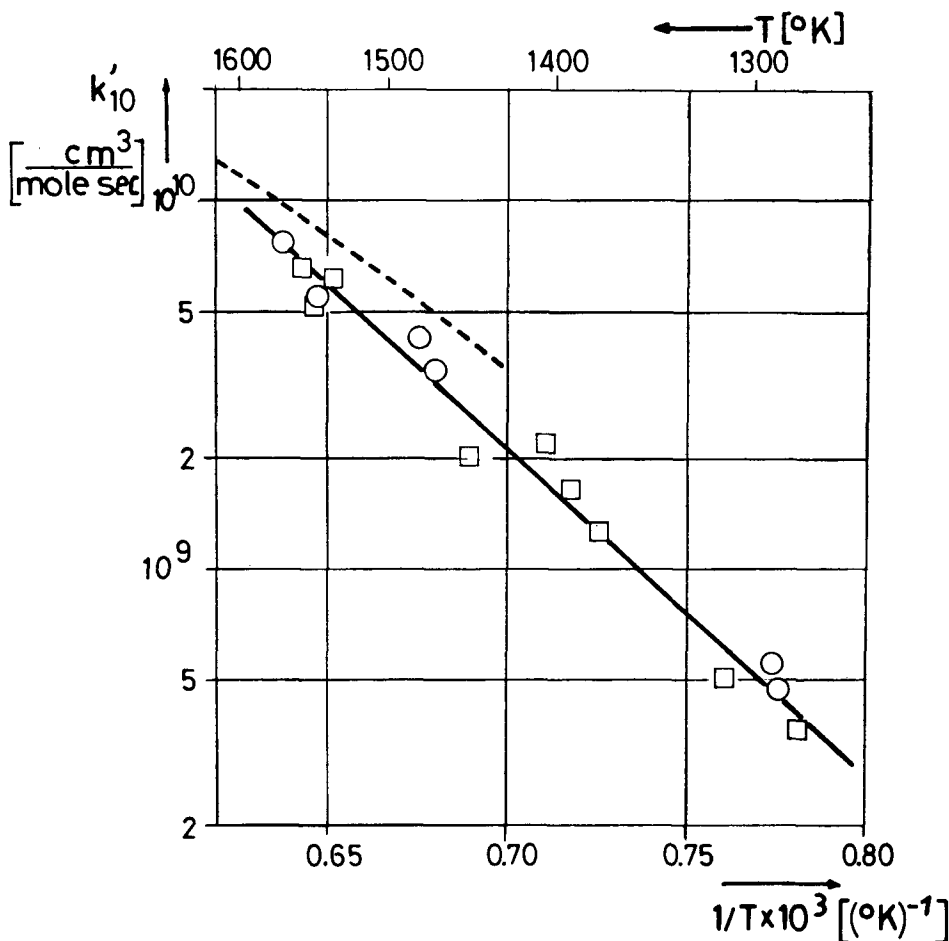$$\times [\text{sec}^{-1}].$$

FIG. 1. N_2H_4 decomposition: low pressure region. $2 \times 10^{-6} \leq [Ar] \leq 6 \times 10^{-6}$ mole/cm³; O, 0.5% N_2H_4 in Ar; □, 0.25% N_2H_4 in Ar. – – – measurements of Diesen (Ref. 2) with $[Ar] = 7 \times 10^{-7}$ mole/cm³ and 0.5%–1% N_2H_4 in Ar.

The increase by a factor of 2 of the rate constant at the highest N_2H_4 concentrations and temperatures around 1100°K would be consistent with mechanisms (1), (2), and (3) mentioned above. It is also consistent with the observation that k'_{10} values are independent of N_2H_4 at $T > 1300°K$ and also with the concentration effects shown in Fig. 2 of Ref. 4. From this we believe, that our k'_{10} and $k'_{1\infty}$ values probably correspond to the rate of the unimolecular reaction. This conclusion can also be drawn from the approximate values for k_2 of about 3×10^{11} cm³/mole sec, at our temperatures, given by Diesen[2] and based on information by Bair.[16] A similar value of about 5×10^{11} cm³/mole sec, within an accuracy of a factor of about 4, can be estimated from our Fig. 2 at about 1200°K, if the observed transition $1 \times k_1$ to $2 \times k_1$ is attributed to the competition

of Reactions (2) and (1). In concluding, it appears rather probable that in the case of N_2H_4, Reaction (2) is much slower than the corresponding reaction $OH + H_2O_2 \rightarrow HO_2 + H_2O$ for H_2O_2 (see below).

Fall-off Curves

The pressure dependence of the first order rate constants of the N_2H_4 decomposition at the lowest applied N_2H_4 concentrations in Ar is shown in Fig. 3. In this figure, our results are compared to the previous shock tube work of Palmer et al.[3] (single-pulse shock tube), of Diesen[2] (mass spectrometric analysis) and of Michel and Wagner[4] (uv absorption technique, also used in our work). The results of Szwarc[1] (flow system with toluene carrier technique) are also given. The measure-
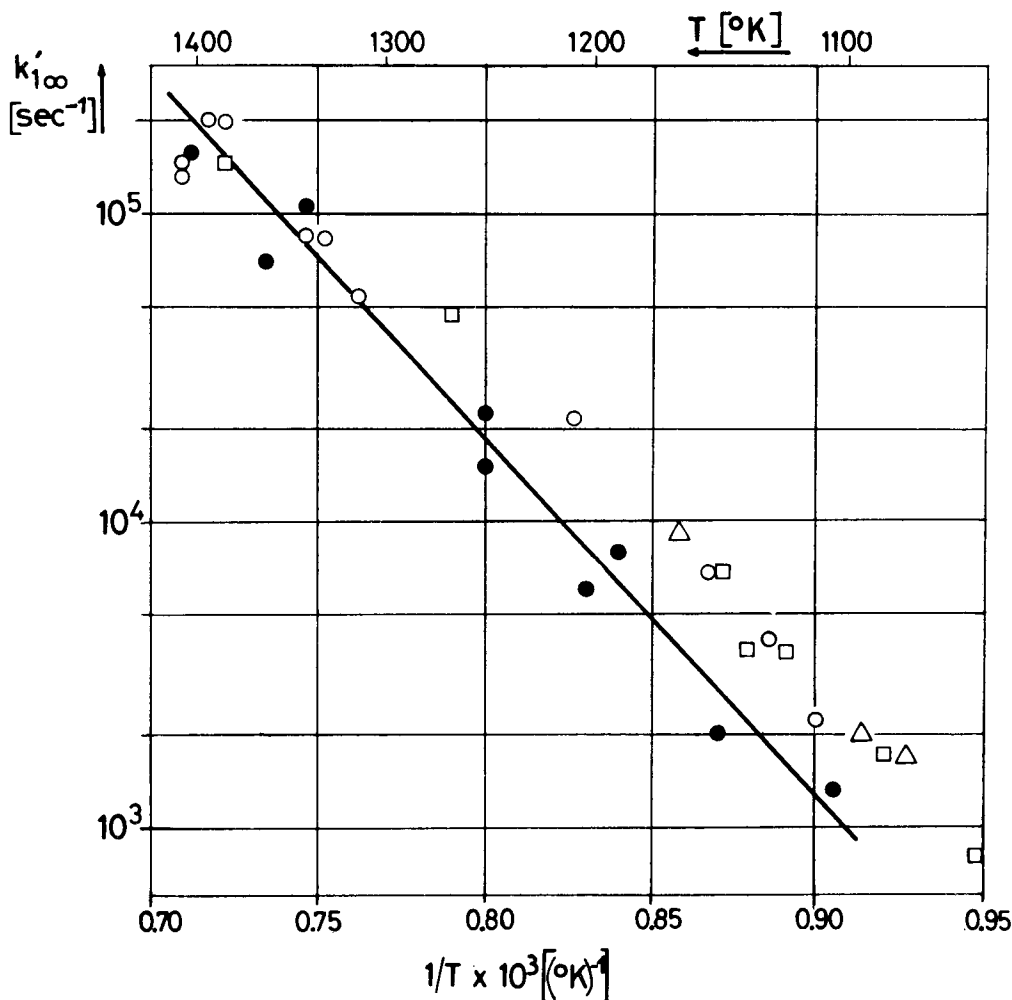
Fig. 2. N_2H_4 decomposition: high pressure region. $10^{-3} \leq$ [Ar] $\leq 3 \times 10^{-3}$ mole/cm³; ●, $[N_2H_4] =$ 1.5–5 $\times$ 10⁻⁸ mole/cm³; ○ $[N_2H_4]$ = 9–14 $\times$ 10⁻⁸ mole/cm³; □, $[N_2H_4]$ = 18–24 $\times$ 10⁻⁸ mole/cm³; △, $[N_2H_4]$ = 40 $\times$ 10⁻⁸ mole/cm³.

ments (Refs. 2, 4 and of this work) have all been carried out at $[N_2H_4] \leq 5 \times 10^{-8}$ mole/cm³; the experiments of Palmer et al.[3] at $10^{-7} \leq [N_2H_4] \leq$ 1.4 $\times$ 10⁻⁶ mole/cm³. Diesen's values are somewhat higher than ours, showing a much lower apparent activation energy. At temperatures where the measurements overlap, this behavior is not confirmed by our measurements. When comparing the more recent results with the measurements of Szwarc,[1] some points must be kept in mind. (Extrapolation from Szwarc's highest temperatures 1050° to 1110°K does not give marked arbitrariness.) First, Szwarc's measurements at $[M] \approx 10^{-7}$ mole/cm³ clearly correspond to the low pressure region of the unimolecular reaction. This has already been pointed out by Gilbert.[17] In addition, Szwarc's activation energy of 60

kcal/mole must be too high, since the low pressure activation energy in this case would be much lower than $E_0 = 55$ kcal/mole (see below). However, the absolute value of Szwarc's experiments gives a reasonable fit with our extrapolation in Fig. 3, if a somewhat higher "collision efficiency" of toluene, used as carrier gas instead of argon, is assumed.

From the experimental fall-off plots in Fig. 3 it cannot be determined whether the limiting rate constants are obtained with, for instance, 5% accuracy. Therefore, theoretical reduced fall-off plots have been calculated for N_2H_4 and compared with the experiments. The number of "effective" oscillators, defined by

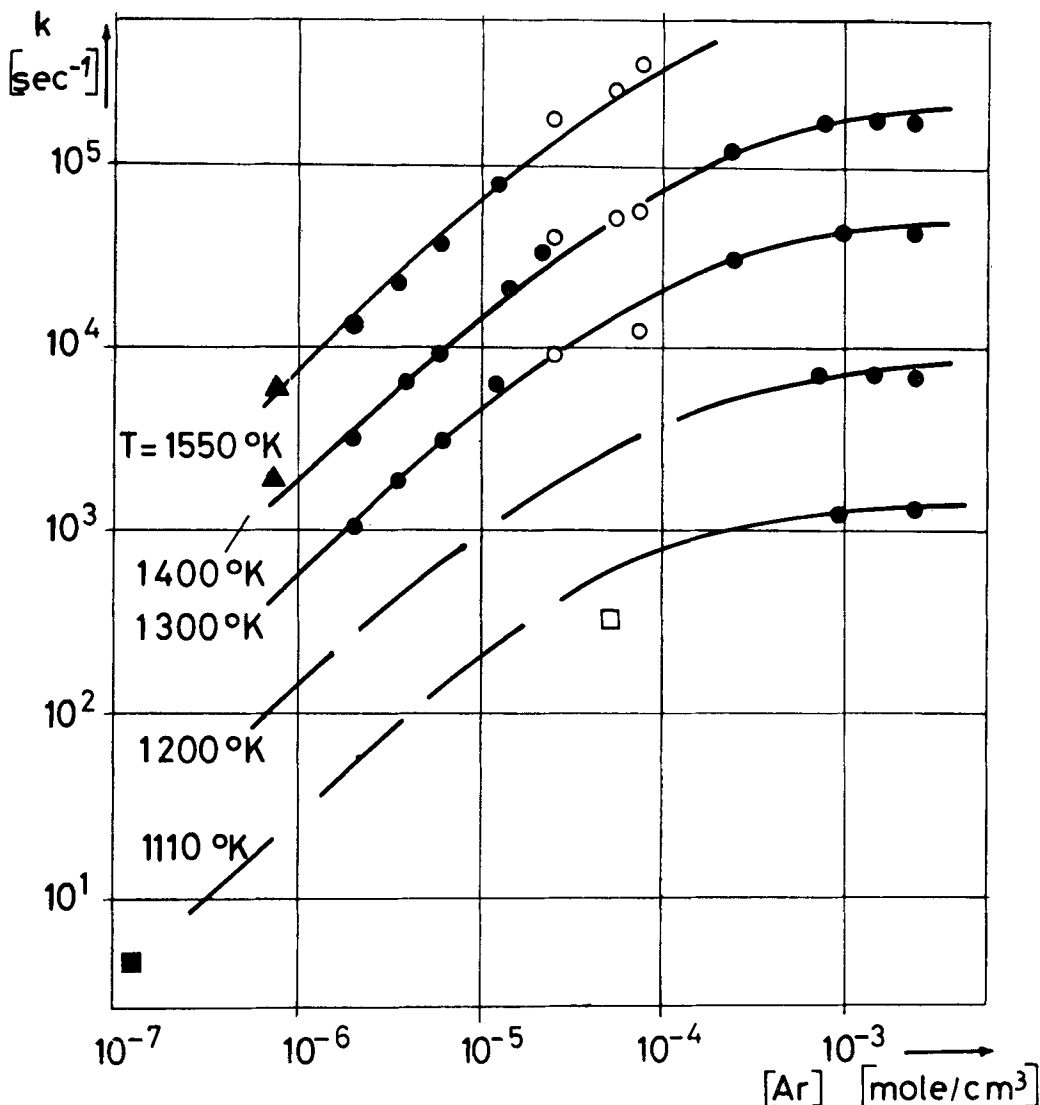$$S_{\mathrm{eff}} = -1/T \left(\partial \ln Q_{\mathrm{vib}} / \partial T^{-1} \right)$$

FIG. 3. N₂H₄ decomposition: fall-off curves. Carrier gas Ar: ●, this work; ○, Ref. 4; ▲, Ref. 2; □, Ref. 3. Carrier gas toluene: ■, Ref. 1.

(Q_{vib} = vibrational partition function), were calculated for different temperatures from the vibrational frequencies of the molecule. Then, by a simplified procedure as described elsewhere,[18] Slater's fall-off curves in reduced form are derived for this S_{eff} and fitted to the experimental fall-off curves. In this way, the solid curves in Fig. 3 are obtained. Inspection of the fall-off curves suggests that the apparent experimental limiting low and high pressure rates $k'_{1\,0}$ and $k'_{1\,\infty}$ are still about 10% below the true limiting values. The apparent activation energies could still vary within 1 kcal/mole, which however is within the experimental accuracy. Therefore,

more realistic limiting rate constants probably are

$$k_{1\,0} = 10^{15.65} \exp\{-[(41 \pm 2)\ \text{kcal/mole}]/RT\}$$
$$\times [\text{cm}^3/\text{mole sec}],$$

at $1280° \leq T \leq 1580°K$ and

$$k_{1\,\infty} = 10^{13.9} \exp\{-[(55 \pm 2)\ \text{kcal/mole}]/RT\}$$
$$\times [\text{sec}^{-1}],$$

at $1100° \leq T \leq 1400°K$.

II. Decomposition of H_2O_2

The homogeneous dissociation of H_2O_2 in flow systems has been investigated previously at temperatures above about 700°K. In several studies,[6–11] summarized by Baldwin and Brattan,[11] the nonchain character of the reaction has been established. The reaction was found to be first order with respect to H_2O_2 and the carrier gas (pressures $\leq$ 1 atm). The different "collision efficiencies" of several carrier gases were measured. These earlier studies can be combined[11] to give an experimental rate constant.
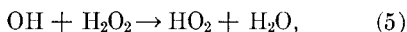
$$k_{II} = 3.4 \times 10^{17} \exp\left[-(46.3 \text{ kcal/mole})/RT\right]$$
$$\times \left[\text{cm}^3/\text{mole sec}\right],$$

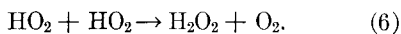between about 710° and 950°K with nitrogen as carrier gas; the rate constants for Ar are 0.67 times smaller.

It is generally accepted that in these studies the unimolecular dissociation

$$H_2O_2 + M \rightarrow 2 \text{ OH} + M, \tag{4}$$

is followed by the rapid reaction

$$\text{OH} + H_2O_2 \rightarrow HO_2 + H_2O, \tag{5}$$

and probably also by

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \tag{6}$$

With quasi-stationary OH and HO_2 concentrations, this gives

$$d[H_2O_2]/dt = -k_{II}[M][H_2O_2]$$

with

$$k_{II} = 2k_4. \tag{7}$$

Thus, the rate constants obtained correspond to twice the rate of the unimolecular reaction near the low pressure limit.

In the present work, H_2O_2 decomposition has been studied in reflected and incident shock waves at temperatures up to 1450°K. At the lowest temperatures and at low pressures, a direct comparison with the flow system results can be given. Thus, the experimental range of rate constants was extended by several orders of magnitude. In addition, information on the high pressure rate constants was obtained.

Experimental Technique

The shock tube equipment was the same as in the low pressure experiments on N_2H_4 decom-

position. Reaction mixtures were prepared by passing Ar through a saturator containing 90%, 95% or 99% H_2O_2 in aqueous solution (Elektrochemische Werke München). During introduction of the reaction gas into the shock tube, part of the H_2O_2 was lost mainly by wall absorption. It was found that the H_2O_2 content of the gas was determined most reliably from its light absorption in the shock wave experiment itself. Normally, H_2O_2 concentrations were 0.07% to 0.15% H_2O_2 in Ar.

The water content from the H_2O_2 solution and from decomposition at the wall during the inlet procedure could only be estimated. However, it seems certain that water impurities were well below 0.5% in Ar.

The decomposition of H_2O_2 behind the shock waves was followed by its light absorption in the ultraviolet region. This absorption is continuous, decreasing at $\lambda \geq 2000$ Å with increasing wavelength.[19] In this range the absorption increases with temperature, slightly around 2300 Å and more strongly at longer wavelengths, e.g. 2900 Å.

In our shock tube measurements, absorption at 2300 Å during the reaction increased at first to a maximum and later decreased to zero absorption [see Fig. 4(a)]. It can be proved that this effect is due to the absorption of a species, which is being formed and consumed again during the reaction. This additional absorption appears to be continuous like the H_2O_2 absorption, but the H_2O_2 absorption extends to longer wavelengths than this additional absorption. At $\lambda = 2900$ Å
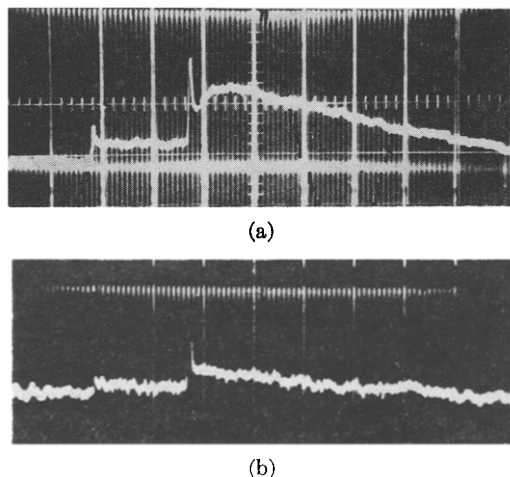

(a)

(b)

FIG. 4. H_2O_2 decomposition behind reflected shock waves. $T = 1060°K$, $[\text{Ar}] = 7.2 \times 10^{-5}$ mole/cm³. (a) Absorption at 2300 Å (absorption hump perhaps due to HO_2). (b) Absorption at 2900 Å. Time marks: 10 μsec, schlieren signals at the front of incident and reflected shock waves.
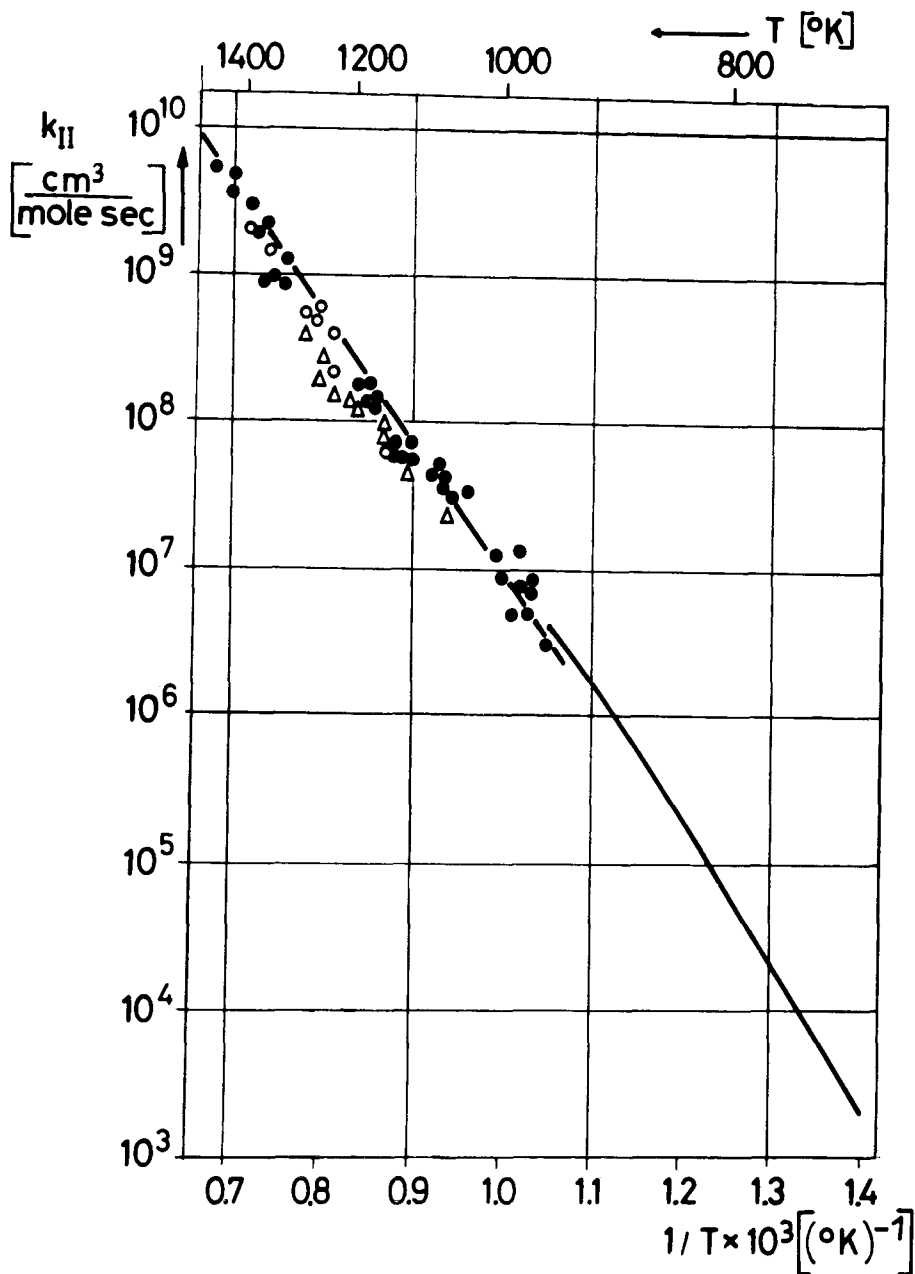
FIG. 5. H₂O₂ decomposition. Measurements at $T \leq 950°K$: Summary by Ref. 11 of flow system results from Refs. 6–11. Measurements at $T \geq 950°K$: Shock tube results, this work, (0.07%–0.15% H₂O₂ in Ar). O, [Ar] = 0.9×10^{-5} to 2×10^{-5} mole/cm³; ●, [Ar] = 4×10^{-5} to 8×10^{-5} mole/cm³; △, [Ar] = 1.8×10^{-4} to 2.4×10^{-4} mole/cm³.

only H_2O_2 absorption is observed [see Fig. 4(b)]. Therefore, all experiments on the H_2O_2 decomposition were carried out using the weak absorption at 2900 Å.

Low Pressure Experiments

Within the experimental accuracy it was found that H_2O_2 decomposes following rate law (7) with $[M] = [Ar] \leq 10^{-4}$ mole/cm³. The experimental rate constants k_{II} are shown in Fig. 5. They can be represented at $950° \leq T \leq 1450°K$ by

$$k_{II} = 10^{15.8} \exp \left[- (40 \text{ kcal/mole})/RT\right]$$

$$[\text{cm}^3/\text{mole sec}].$$

Measurements from reflected shock waves at $[Ar] \approx 4\text{-}8 \times 10^{-5}$ mole/cm³ and from incident shock waves at $[Ar] \approx 1 \times 10^{-5}$ mole/cm³ give the same results.

The low temperature flow system results are shown together with our measurements in Fig. 5. They have been converted from N_2 to Ar as carrier gas, using Baldwin's[11] collision efficiencies, $1:0.67$. The measurements agree reasonably well; only a slight shift is observed at $T \approx 950°K$. This shift may be due in part to the neglect of the small water contents of the gas in calculating the shock wave data: $[\Delta T^{-1} \leq +0.01 \times 10^{-3} (°K)^{-1}]$. In interpreting our experimental results, it seems clear, that consecutive reactions (5) and (6) double the rate of (4) at temperatures $T \approx 1000°K$: $k_{II} \approx 2 \times k_4$. However, it seems probable that at higher temperatures ($T \approx 1400°K$) $k_{II} \approx 1 \times k_4$. Then, assuming $k_{II} \approx 1 \times k_4$ at 1450°K, and $k_{II} \approx 2 \times k_4$ at 950°K,

$$k_{4\,0} = 10^{16.5} \exp \left[- (43 \text{ kcal/mole})/RT\right]$$

$$[\text{cm}^3/\text{mole sec}]$$

is obtained.

Medium Pressure Experiments

In Fig. 5 a systematic decrease of k_{II} is observed at $[Ar] \approx 2 \times 10^{-4}$ mole/cm³ (pressure $\approx$ 20 atm). This effect probably cannot be explained by experimental errors, but may correspond to the transition of the rate constant to the high pressure region. As the measurements could not be extended to markedly higher pressures (due to too weak absorption of H_2O_2 at 2900 Å), the limiting rate constant was estimated. This was done as described in I by fitting calculated fall-off curves to the factor 1.8 decrease of k_{II} at 1200°K and

2×10^{-4} mole/cm³. This gives $k_{II\,\infty} = 2k_4 \approx 6 \times 10^{-4}$ sec⁻¹ and if represented in the form $k_{4\,\infty} = A_\infty \exp (-E_0/RT)$ with $E_0 = 49.6$ kcal/ mole, $A_\infty \approx 10^{13.5}$ sec⁻¹. This estimate represents at least a lower limit for $k_{4\,\infty}$.

Mechanism. Formation of HO_2

The OH concentration cannot be regarded as quasistationary for all conditions considered. Applying the data of Baldwin et al.[20-22] to k_5/k (OH + H_2) and the value given by Greiner[23] one obtains

$$k_5 \approx 10^{13.1} \exp \left[- (2 \text{ kcal/mole})/RT\right]$$

$$[\text{cm}^3/\text{mole sec}].$$

Neglecting other consecutive reactions, quasistationary values are obtained for OH of

$$[\text{OH}]_{\text{qu st}} = (2k_4/k_5)[Ar] \approx 2 \times 10^{-6}[Ar]$$

at 1000°K and $2 \times 10^{-3}[Ar]$ at 1450°K. Thus, at 1450°K the value of $[\text{OH}]_{\text{qu st}}$ would be of the order of the initial H_2O_2 concentration. Therefore, it seems reasonable to assume that around 1400°K. the value $k_{II} \approx 1 \times k_4$ in contrast to temperatures around and below 1000°K, where $k_{II} \approx 2 \times k_4$. Taking this into account one finally obtains

$$k_{4\,0} = 10^{16.5} \exp \left[- (43 \text{ kcal/mole})/RT\right]$$

$$[\text{cm}^3/\text{mole sec}],$$

for $950° \leq T \leq 1450°K$.

During H_2O_2 decomposition, HO_2 is formed via Reaction (5) and consumed by Reaction (6) and possibly by

$$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2, \qquad (8)$$
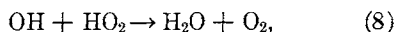
or by dissociation of HO_2. Rates ($T = 300°K$) for $k_8 \geq 6 \times 10^{12}$ cm³/mole sec are given by Kaufman[24] and for $k_6 \approx 1.8 \times 10^{12}$ cm³/mole sec by Baldwin et al.,[20] Schofield,[22] and Foner and Hudson.[25] Dissociation of HO_2 should be slower than of H_2O_2.

$[HO_2]$ can be estimated using the data for Reactions (4), (5), (6), and (8). Whereas $[OH]$ can be treated as quasistationary up to $T \leq$ 1300°K under the experimental conditions, this is not valid for $[HO_2]$ at $T \geq 1000°K$. Integration of the rate equations, using the given rate constants, yields a maximum concentration of the

order of 5% of the H$_2$O$_2$ concentration at 1000–1100°K. Therefore, compared to other systems, high relative HO$_2$ concentrations are to be expected.

In the following, it is assumed that the additional absorption (A) at 2300 Å [see Fig. 4(a)] is due to HO$_2$. This hypothesis is confirmed by the observations of Ref. 38, and also consistent with the following experimental checks (range of temperatures $1000° \leq T \leq 1300°K$):

a. With $[OH] \approx 0$, the initial rate of HO$_2$ formation is given by

$$(d[HO_2]/dt)_{t=0} = 2k_4[H_2O_2]_{t=0}[Ar].$$

If we assume that the temperature dependence of the HO$_2$ absorption coefficient is small around 2300 Å, the quantity

$$([H_2O_2]_{t=0}[Ar])^{-1} (dA/dt)_{t=0},$$

should be approximately proportional to k_4 ($A =$ additional absorption at 2300 Å). This is in agreement with experimental observations and makes it possible to determine the absorption coefficient of HO$_2$. (In practice, the $A(t)$ profiles were fitted to HO$_2$ concentration profiles obtained by integration of the rate equations.)

b. Thus, by calibrating HO$_2$ absorption via the initial rate, the maximum concentrations can be determined from the maximum of A (see Fig. 4). These experimental values agree with calculated maximum HO$_2$ concentrations within a factor of 2. In particular, these concentrations show approximately the predicted increase with temperature. Complete agreement can be obtained by slightly adjusting the rate constants k_6 and k_8.

c. The time required to reach maximum HO$_2$ absorption agrees in the calculations within a factor of 2.

d. The rate of HO$_2$ consumption was experimentally found to be of the order of $\frac{1}{2}k_{II}$, in reasonable agreement with the calculations. Further checks are underway.[26]

III. Unimolecular Reactions

Low Pressure Region

It has been shown by Troe and Wagner[18] that nonequilibrium theories of unimolecular reactions give better fits of the experimental data of the low pressure region, especially for small molecules, than the strong collision model. The following expression has been derived for the low pressure limiting rate constant:

$$k_0 \approx Z[\rho_{vib}(E_0)/Q_{vib}(T)] \exp(-E_0/RT)A(T), \quad (9)$$

with

$$A(T) = A_{anh}A_{rot}A_ZRT$$
$$\times [1 + (\sqrt{2} RT/\langle\Delta E^2\rangle^{1/2})]^{-2}, \quad (10)$$

$[Z =$ gas kinetic collision number, $\rho_{vib}(E_0) =$ density of vibrational states at E_0, $Q_{vib}(T) =$ vibrational partition function, $\langle\Delta E^2\rangle =$ mean square energy, transferred in collisions of molecules near E_0. $A_{anh}A_{rot}A_Z =$ correction factor for anharmonicity, rotation and deviations of the normalization collision number from Z].

Formulas (9) and (10) contain the strong collision HKRRM theory as a limit for $\langle\Delta E^2\rangle \gg (RT)^2$. For $\langle\Delta E^2\rangle \ll (RT)^2$, diffusion theories of the low pressure region[27,28] are approached. Formulas (9) and (10) are, of course, simplified expressions and are far from giving a complete description of the low pressure rate constant. However, it seems to be a useful starting point for an interpretation.

Z was estimated with $\sigma \approx 4.5$ Å: $Z(1300°K) = 4.8 \times 10^{14}$ cm^3/mole sec. E_0 values are 49.6 kcal/mole for H$_2$O$_2$[29] and ≈ 55 kcal/mole for N$_2$H$_4$ (see below). In calculating the density of states and the partition function, the hindered rotator of H$_2$O$_2$ around the O–O-axis has to be taken into account. Its density of levels was calculated and combined with the contribution of the five oscillators (see Appendix). The different numbers of oscillators of H$_2$O$_2$ and N$_2$H$_4$ (frequencies taken from Refs. 30, 33, 34) give quite different $\rho_{vib}(E_0)/Q_{vib}$ values: $2 \times 10^2/$(kcal/mole) and $3.3 \times 10^4/$(kcal/mole), respectively, at $T = 1300°K$. If the experimental constants k_{10} and k_{40} are written in the form (9), with these molecular properties, one derives $A(1300°K) \approx 4$ kcal/mole (H$_2$O$_2$) and ≈ 0.06 kcal/mole (N$_2$H$_4$). This large difference represents about the maximum spread in experimental $A(T)$ values of a large number of examples.[18] It shows, that, in addition to $\langle\Delta E^2\rangle$ not only ρ_{vib}/Q_{vib}, but $A_{anh}A_{rot}A_Z$ probably plays an important role. This contribution has not yet been adequately described.

It was shown[18] that the apparent activation energies E_{a0} of most experimental examples can best be fitted by an expression

$$E_{a0} \approx E_0 + R[(\Delta \ln Q_{vib}/\Delta T^{-1})$$
$$- \tfrac{1}{2}(\Delta \ln T/\Delta T^{-1})]. \quad (11)$$

For our temperature ranges, this gives ≈ 45 kcal/mole (H$_2$O$_2$) and ≈ 42 kcal/mole (N$_2$H$_4$), in good agreement with the experiments.

High Pressure Region

The appropriate expression for a discussion of the high pressure rate constant k_∞ is the formula of the transition state theory

$$k_\infty = (kT/h)(Q^\ddagger/Q) \exp(-E_0/RT)$$
$$= A_\infty \exp(-E_0/RT). \quad (12)$$

The difficulty of applying this formula to the experiments consists in the correct choice of the activated complex. Therefore, in the following some estimates for different complexes are given. Representing $Q^\ddagger/Q$ initially by the reciprocal partition function of the oscillator corresponding to the N–N or O–O stretching vibrations, one obtains $A_\infty(1200°\text{K}) = 10^{13.2} \text{ sec}^{-1}$. This quantity is slightly temperature-dependent and contributes about $\frac{1}{2}RT$ to the activation energy near $1200°\text{K}$. The experimental A_∞ values are higher, indicating a looser activated complex. Additional conversion of the O–O and N–N torsional vibration into a free internal rotation in the activated complex increases A_∞ to A_∞ $(1200°\text{K}) = 10^{13.5} \text{ sec}^{-1}$ (N_2H_4) and $10^{13.4} \text{ sec}^{-1}$ (H_2O_2).

Inclusion of the overall rotation results in a further increase of A_∞. Roughly estimating the mean N–N or O–O distance of activated complexes to be twice the equilibrium values gives an increase of A_∞ by a factor of 4. This contribution especially needs to be refined.

The experimental high pressure activation energy is estimated to agree with E_0 within an accuracy of about RT. Therefore, from our experiments, $D(\text{H}_2\text{N–NH}_2) = 55 \pm 2$ kcal/mole. Combining this with other data,[29] one obtains $\Delta H_{f0}°(\text{NH}_2) = 40.5 \pm 1$ kcal/mole and $D(\text{H–NH}_2) = 101.5 \pm 1$ kcal/mole.

Extrapolation of $k_{1\infty} \propto \exp(-E_0/RT)$ to room temperature and conversion to a recombination rate constant[29] gives good agreement with second order recombination results.[35] The corresponding extrapolation of k_{10} according to formula (11) indicates a transition between second and third order recombination at pressures of the order of 1 mm Hg. The shift of the transition region to low pressures when going from $1300°$ to $300°\text{K}$ is very pronounced. A corresponding extrapolation of k_{40} according to formula (11) and comparison with third order recombination results[36,37] again gives agreement within a factor of 2.

Appendix

Internal rotator of H_2O_2 [30]: $V(\chi) = V_1 \cos\chi + V_2 \cos 2\chi$, $V_1 = 1.43$ kcal/mole, $V_2 = 1.07$ kcal/

mole. Density of states:

$$\rho_4(E) = (8\pi^2\theta/h^2 N_L E)^{1/2}$$
$$\times (2\pi)^{-1} \int_0^{2\pi*} [1 - V(\chi)/E]^{-1/2} d\chi$$

θ = effective moment of inertia of one rotating OH group, see Ref. 31.

$\int^*$ = integration over all χ with $V(\chi) \le E$.

$$Q_4 = (8\pi^3\theta kT/h^2)^{1/2}\pi^{-1} \int_0^\pi \exp[-V(\chi)/RT] d\chi.$$

Density of states of the whole molecule:

$$\rho_{\text{vib}}(E) \approx (d/dE) \int_0^{E+aE_z} \rho_{1,6}(E_1) dE_1$$
$$\times \int_0^{E+aE_z-E_1} \rho_4(E_4) dE_4$$

with

$$\rho_{1,6}(E_1) = (E_1 + aE_z)^{s*-1}/(s*-1)!\pi\epsilon_i,$$
$$s* = 5, \quad E_z = \tfrac{1}{2}\sum\epsilon_i,$$

ϵ_i = Eigenenergies of the five oscillators[30] 1, 2, 3, 5, 6.
a = correction factor.[32]

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COMMENTS

H. B. Palmer, Pennsylvania State University. It is gratifying to see this detailed study of the pressure dependence of hydrazine decomposition, and to find in it a confirmation of the main features of the reactions that we proposed at the Tenth Symposium. Agreement on the high-pressure activation energy is within 1 kcal mole⁻¹. Our high-pressure pre-exponential factor was apparently about a factor of 2 low, but the pressure fall-off parameters are in remarkable agreement. The pressure dependence implicit in our determination defines a curve of k-versus-p running essentially parallel to that of Meyer et al. throughout its entire course. The time has now clearly arrived to push on to higher relative concentrations of hydrazine, to study the secondary reactions, and to approach the problem of the hydrazine flame in the new spirit exemplified by the numerous computer studies of flames presented at this Symposium.