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DISSOCIATION RATES OF SHOCK-HEATED BROMINE IN PRESENCE OF HELIUM AND XENON

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16. Abstract

The rates of dissociation of bromine (Br_2) in the presence of helium (He) and xenon (Xe) were measured behind the incident shock. The light absorption technique was used to measure Br_2 concentration. The temperature range was 1200 to 1950 K. In addition, an indication of the efficiency of Br_2 itself as a collision partner was determined and used in the data reduction of the 1-percent-Br_2 - noble-gas mixtures. Also included in the data reduction were corrections for the effects of boundary layer buildup. The following rate constants were determined:

$$k_{D,\mathrm{He}} = (2.15\pm0.86)\times10^{11}\, T^{1/2} \exp\left[(-31.9\pm1.2 \text{ kcal/mole})/RT\right] \quad \mathrm{cm^3/(mole)(sec)}$$

$$k_{D,\mathrm{Xe}} = (6.92\pm1.73)\times10^{11}\, T^{1/2} \exp\left[(-35.5\pm0.7 \text{ kcal/mole})/RT\right] \quad \mathrm{cm^3/(mole)(sec)}$$

where T is the absolute temperature, and R is the gas constant.

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DISSOCIATION RATES OF SHOCK-HEATED BROMINE IN PRESENCE OF HELIUM AND XENON

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SUMMARY

The rates of dissociation of bromine (Br_2) in the presence of helium (He) and xenon (Xe) were determined in a shock tube. All rate measurements were made behind the incident shock using the light absorption technique to measure Br_2 concentration. The temperature range covered was 1200 to 1950 K. In addition, an indication of the efficiency of Br_2 itself as a collision partner was determined from a comparison of bromine dissociation rates in two Xe-Br_2 mixtures containing different Br_2 concentrations. Molecular bromine was 3.8 times as effective as xenon at 1250 K, dropping to 1.5 times as effective at 1900 K.

The effects of boundary layer buildup were included in the data reduction. Mirels' laminar boundary layer theory was used to correct the initial slope measurements. Calculations indicated that these initial slope measurements had been made while the boundary layer was still laminar. The most significant effect of boundary layer on the dissociation rate constant k_D was to lower the activation energy E_a(1 percent for $k_{D,Xe}$ and 5 percent for $k_{D,He}$) calculated from the experimental data.

The activation energies (35.5 kcal/mole for $k_{D.Xe}$ and 31.9 kcal/mole for $k_{D,He}$) are well below the bond dissociation energy for Br_2. This is consistent with previous studies by this investigator of Br_2 dissociation in the presence of neon (Ne), argon (Ar), and krypton (Kr), as well as with diatomic dissociation results of others. Nevertheless, it is a puzzling result for which no satisfactory explanation has thus far been made.

INTRODUCTION

The efficiencies of molecules in the two-body dissociation of diatoms, and as third bodies in the related process of bimolecular association, continue to attract interest.

In recombination, the molecule formed by the association of atoms is stabilized through the removal of energy by the third body. In dissociation, the collision of the diatom with another species causes the diatom to dissociate. Experimental information on the effects of the collision partner helps shed light on the nature of the chemical kinetic mechanism of dissociation-recombination.

Historically, experiments on third-body efficiencies in recombination were done before the dissociation experiments. The most detailed of these have studied halogen recombination in the presence of various third bodies (refs. 1 to 3).

In the last 12 years, modern shock-tube technology has been used to study dissociation, expecially of diatoms (refs. 4 to 15). These experimental results have heightened interest in the theory of dissociation-recombination. In recent years, several theoretical models have been proposed for the mechanism. However, proper evaluation of these models and further progress in these areas have been hampered by two problems. First, insufficient experimental data are available. Second, shock-tube measurements of rate constants have often been imprecise.

Reference 8 describes an investigation of bromine dissociation rates in the presence of argon, neon, and krypton. In this work, a successful effort had been made to overcome experimental problems that had plagued past investigators.

The present work extended the mass range of Br_2 collision partners to helium and xenon. The Br_2 dissociation rates in He-Br_2 and Xe-Br_2 mixtures were measured. This makes available, for the first time, data on the effectiveness of all five nonradioactive noble bases in causing Br_2 dissociation.

Most previous investigations ignored the special contribution of Br_2-Br_2 collisions to the bromine dissociation. However, in recombination at room temperature, Br_2 is 100 times as efficient as Ar (ref. 3). If it had turned out in dissociation that Br_2 were many times as efficient as Ar, then even in 1-percent Br_2 mixtures, serious errors would have resulted from ignoring Br_2-Br_2 collisions. Conclusions regarding noble gas collision partner efficiencies might then be meaningless. Therefore, an indication of the efficiency of Br_2 ifself as a collision partner has also been determined in the present work.

EXPERIMENTAL CONSIDERATIONS

Many of the experimental details have appeared in previous reports (refs. 8 and 16); therefore, this experimental discussion will only be a brief summary of essentials.

Shock Tube

In designing the shock-tube apparatus, a systematic effort was made to avoid all contact of bromine with metal surfaces. The importance of this was stressed in references 8 and 16. Glass, tetrafluoroethylene polymer (TFE), and polyethylene terephthalate were the only materials to contact bromine in the shock tube.

The main components of the shock tube were a 6-foot (1.8288-m) driver section made of stainless steel and a 10-foot (3.048-m) driven or test section made of borosilicate glass pipe. Each section had an inner diameter of 4 inches (10.16 cm).

The shock waves were initiated by piercing the diaphragms. Before the piercing, the pressure of the helium driver gas was raised to within 3 psi (2.07×10^4 N/m^2) of the diaphragm bursting pressure to ensure rapid opening. Mach number and temperature variations were produced by varying the initial driven gas pressure.

Gas Mixtures

Calibrated Bourdon tube gages were used to prepare the bromine-noble gas mixtures by the partial pressure method. Reagent grade bromine (99.5 percent minimum purity) was further purified by distillation before it was used. The gas purities were as follows: helium, 99.9997 percent; xeon, 99.996 percent.

Instrumentation

Concentrations were determined by the optical absorption method. The incandescent light source (6.5 V, 2.75 A), powered by a highly regulated power supply, was very stable. A fixed 2.5×10^{-2}-inch (0.635-mm) slit limited the width of the light beam entering the shock tube. The light emerging from the shock tube passed through an interference filter that fed monochromatic light into the 931A photomultiplier. The measured peak and bandwidth at the filter half-peak were 4400 and 80 Å ($\times 10^{-10}$ m), respectively. The high voltage required to operate the photomultiplier was produced by a very stable power supply (0.01-percent change/hr). The photomultiplier output was displayed on a dual-beam oscilloscope and photographed. The uncertanity in the value of the incident light intensity I_0 for the shocked gas was within ±0.5 percent. More complete details on the efforts made to keep I_0 within narrow bounds are given in reference 8.

Two additional light beams together with associated optical equipment (like that just described) were located 6 inches (15.24 cm) on either side of the light that was used to measure bromine concentration. Photomultiplier signals from these light beams were used to measure shock velocity. The first beam crossed by the incident shock was used to trigger the oscilloscope.

RESULTS

Calculations

The rate constant for the dissociation of bromine

$$Br_2 + M \underset{k_R}{\overset{k_D}{\rightleftharpoons}} 2Br + M \tag{1}$$

is defined by

$$\frac{-d[Br_2]}{dt} = k_D[Br_2][M] \tag{2}$$

(All symbols are defined in the appendix.) No contribution from the reverse reaction appears in equation (2) since only initial rates were measured in this experiment. In cases where there are multiple collision partners, the following relation is assumed:

$$\frac{-d[Br_2]}{dt} = k_{D,A}[Br_2][A] + k_{D,B}[Br_2][B] + \ldots \tag{3}$$

where $k_{D,M}$ is the rate constant in an infinitely dilute solution in collision partner M.

The collision partner can be Br_2, Br, or any inert species present. Various investigators have used equation (3) (refs. 9 and 12). In each case, they stated that the relation expressed by equation (3) is an unproved assumption. The actual rate-governing equation may be more complex. However, for Br_2 mixtures greatly diluted by noble gases, one would expect equation (3) to apply (see ref. 17).

For the initial slope method, equation (4) expresses k_D in terms of quantities that are either measurable or calculable:

$$k_D = \frac{\left(\frac{dI_2}{d\tau}\right)\left(\frac{V_2}{V_1}\right)F}{I_0\left(\frac{I_2}{I_0}\right)\epsilon_2 S[Br_2][M]} \tag{4}$$

The expression makes use of the enthalpy correction factor F of Palmer and Hornig (see refs. 9 and 12). As dissociation proceeds, the gas cools and all gas properties change. The initial slopes are affected by these changes. They are not the slopes at constant temperature and pressure. The enthalpy correction for each run established the rate constant at the initial shocked gas conditions.

Effects of Boundary Layer Buildup

Recent shock-tube publications have given some consideration to the effects of boundary layer buildup on rate measurements (refs. 14, 15, and 18). Heightened interest in boundary layer in shock tubes has been prompted by the theoretical work of Mirels (ref. 19).

Mirels (ref. 19) applied a procedure (previously developed by him in refs. 20 and 21) to calculate the variations of shock-tube flow properties resulting from boundary layer buildup. The growing boundary layer creates, in effect, a diverging duct inside the shock tube through which the shocked gas flows subsonically. This tends to produce increases in pressure, temperature, and density, and a decrease in fluid particle velocity. The decreasing velocity affects the particle time-of-flight, or reaction time.

These boundary layer effects on gas properties and time are particularly important for chemical rate studies. A knowledge of the true reaction time and the local state of the gas is essential.

An earlier report (ref. 22) of mine described a method for determining the effects of boundary layer buildup on shock-tube rate measurements. The method was designed for use with the initial slope technique of rate determination, which has been used herein for all bromine rate measurements. Calculation of the transition from laminar to turbulent boundary layer using published experimental data (ref. 23) indicated that the bromine measurements were made while a laminar boundary layer existed in the tube. Consequently, the laminar boundary layer relations were used (ref. 20).

Measured Rate Constants

With the aid of equations (3) and (4) and Mirels' boundary layer relations, bromine dissociation rate constants were calculated for the 1-percent-Br_2 - 99-percent-Xe and the 1-percent-Br_2 - 79-percent-Xe mixtures. The 20-percent Xe was required in the Br_2-He mixture to enable sufficiently strong shocks to be produced within the pressure limitations of the shock tube. The rate data are plotted in the traditional Arrhenius manner, log k_D against 1/T. Experimental points for $k_{D,Xe}$ are in figure 1 while those for $k_{D,He}$ are in figure 2. In each case, the solid line represents the least-squares fit of the experimental points. The dotted lines represent the data corrected for boundary layer buildup.

Figure 3 presents the rate data for the experiment at a higher Br_2 concentration (3-percent Br_2 - 97-percent Xe). The dissociation experiment was run in order to gain an indication of the Br_2-Br_2 contribution to the overall dissociation. With the use of equation (3), the ratio $k_{D,Br_2}/k_{D,Xe}$ was easily obtained by comparing, at any temperature, the overall dissociation rate constant for this mixture to that of the 1-percent-Br_2 - 99-percent-Xe mixture.

As was expected, the efficiency of Br_2 was not so much greater than that of either Xe or He to be very significant at the 1-percent bromine concentration. At 1250 K, the results indicate that Br_2 is 3.8 times as efficient as Xe in dissociating another molecule of bromine. At 1900 K, the relative efficiency reduces to 1.5. Ignoring the higher efficiency of Br_2 would only have introduced errors of 3 percent or less in the rate constants.

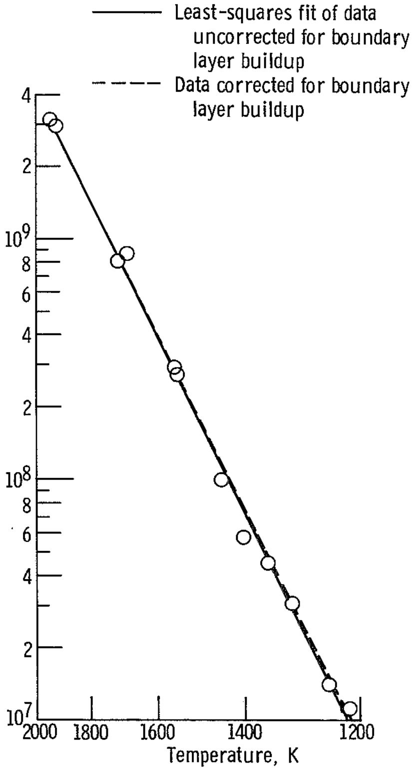

Figure 1. - Rate constants for dissociation of bromine - 1-percent-bromine - 99-percent-xenon mixture.

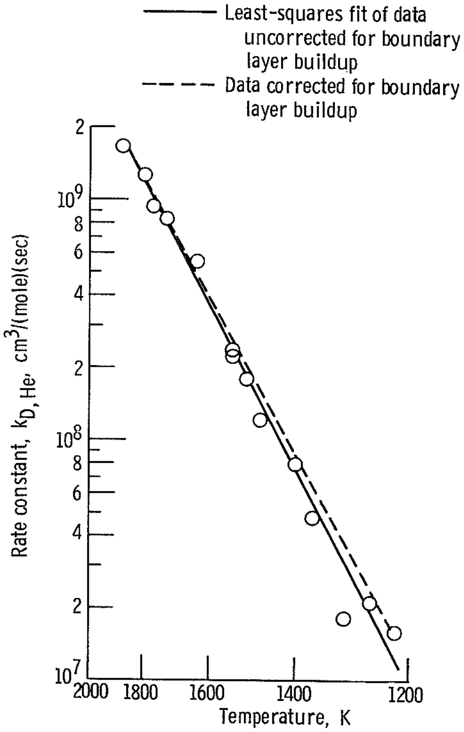

Figure 2. - Rate constants for dissociation of bromine - 1-percent-bromine - 20-percent-xenon - 70-percent-helium mixture.

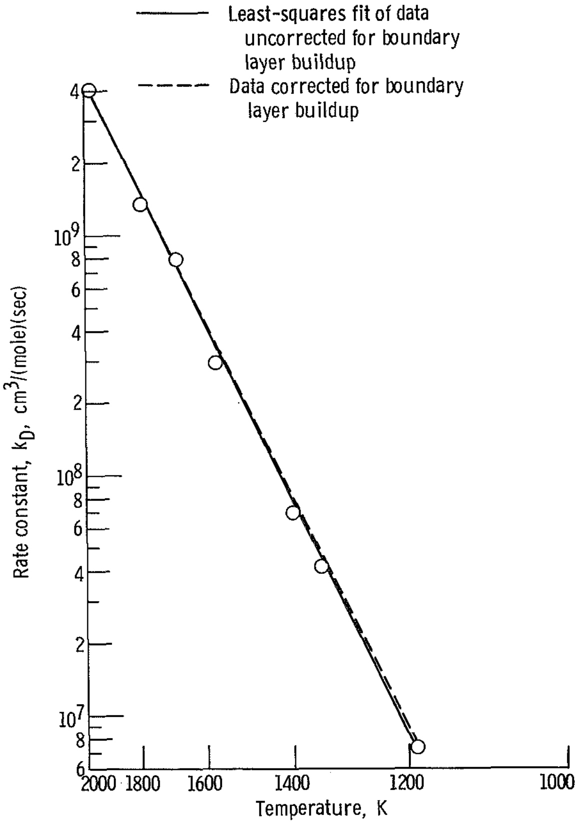

Figure 3. - Rate constants for dissociation of bromine - 3-percent-bromine - 97-percent-xenon mixture.

The rate constant equations expressing the temperature dependencies of $k_{D,Xe}$ and $k_{D,He}$ in the simple collisional form, $AT^{1/2} \exp(-E_a/RT)$, are

$$k_{D,He} = (2.15 \pm 0.86) \times 10^{11}\ T^{1/2} \exp[(-31.9 \pm 1.2\ kcal/mole)/RT] \quad cm^3/(mole)(sec) \tag{7}$$

$$k_{D,Xe} = (6.92 \pm 1.73) \times 10^{11}\ T^{1/2} \exp[(-35.5 \pm 0.7\ kcal/mole)/RT] \quad cm^3/(mole)(sec) \tag{8}$$

DISCUSSION

The activation energy E_a for the rate of dissociation of Br_2 is less than its dissociation energy D_0 for the rate equation in the simple collisional form. The dissociation energy for Br_2 is 45.5 kilocalories per mole. However, in no case was E_a close to

45.5 for any of the systems investigated (see eqs. (7) and (8)). These Br_2 dissociation rate results are consistent with this investigator's previous results for Ne-Br_2, Ar-Br_2, and Kr-Br_2 (ref. 8). Furthermore, all other bromine absorption experiments (refs. 7 to 10, and 12), as well as the recent emission experiments (refs. 14 and 15), have reported E_a to be less than D_0. Finally, other published data, for polyatomic as well as diatomic species, found $E_a < D_0$ (refs. 6, 10 to 13, and 24).

Over the past few years, various authors have tried to understand and explain this paradoxical result. Some authors have expressed some suspicion of the experiments, especially since all were done in a shock tube.

Surely it does not take less energy to dissociate a diatomic molecule than to break its diatomic bond! Consequently, it was felt that the shock-tube data must have some consistent bias or else an important shock-tube effect has been overlooked. The neglecting of the effects of boundary layer buildup in shock tubes is of this type. However, the present investigation revealed this correction of the rate data to be in the opposite direction. It makes the activation energies even lower. The boundary layer corrections resulted in a 1-percent decrease in the E_a of $k_{D,Xe}$ (fig. 1) and a 5-percent decrease in the E_a of $k_{D,He}$ (fig. 2).

Another approach to explaining this apparent paradox has been taken by Palmer and Hornig (ref. 9), Benson (ref. 25), and others. Benson answers the paradox by taking a closer look at what is actually meant by the activation energy. He points out that a reacting molecule has a certain amount of internal thermal energy (such as vibrational). Immediately following dissociation, if the molecular fragments retain the same amount of internal energy, then $E_a = D_0$. The activation energy for the reaction at temperature T would be precisely the same as the value at absolute zero. If, to the contrary, the fragments have less energy than the nonreacting molecule, then $E_a < D_0$.

Palmer and Hornig (ref. 9) were on the same track when they considered the possibility that degrees of freedom other than the relative motion of a colliding pair along the line of centers may contribute energy for dissociation. The term $(D_0/RT)^{m-1}$ was included in the rate expression. This is the well-known classical approach to the inclusion of the effects of internal modes (ref. 26). Unfortunately, the exponent m corresponded to more classical square terms than seemed possible.

The discrepancy between E_a and D_0 has been attributed to vibration-dissociation coupling by some kineticists (refs. 27 and 28). However, attempts to demonstrate this have not been successful thus far. This problem remains unresolved.

The Mirels theory, which was used in this report to make the boundary layer corrections, is controversial. Based on experimental measurements on shocked gas flow accompanied by laminar boundary layer buildup, Fox, McLaren, and Hobson (ref. 29) concluded that Mirels' theory gives an adequate description of the flow. However, in another laminar experiment (ref. 30), the Mirels' formula did not fully describe the results. Conflicting reports on the applicability of Mirels' boundary layer theory were also made at the Seventh Shock Tube Symposium (ref. 31). Depending on the shocked gas variable followed, some authors expressed confidence in Mirels' theory while others found it wanting.

However, this controversy has no important bearing on the present work. The boundary layer corrections of the rate constants were not large. No essential features of the results were changed by applying the corrections. For example, the conclusion that the activation energy is far below the Br_2 dissociation energy holds both for the uncorrected and the corrected activation energies. Finally, the use of the data for evaluating dissociation-recombination theories will not hinge on the correctness of the Mirels' layer corrections.

SUMMARY OF RESULTS

The rates of dissociation of bromine (Br_2) in the presence of helium (He) and xenon (Xe) were measured behind the incident shock. The second-order rate constant for Br_2 dissociation resulting from Br_2-He collisions is

$$k_{D,He} = (2.15\pm0.86)\times10^{11}\ T^{1/2}\ \exp\left[(-31.9\pm1.2\ \text{kcal/mole})/RT\right] \qquad \text{cm}^3/(\text{mole})(\text{sec})$$

where T is the absolute temperature and R is the gas constant. The rate constant for Br_2 dissociation resulting from Br_2-Xe collisions is

$$k_{D,Xe} = (6.92\pm1.73)\times10^{11}\ T^{1/2}\ \exp\left[(-35.5\pm0.7\ \text{kcal/mole})/RT\right] \qquad \text{cm}^3(\text{mole})(\text{sec})$$

Molecular bromine was less than four times as effective as Xe in Br_2 dissociation over the temperature range investigated, 1200 to 1950 K. Therefore, in the 1-percent-Br_2 - 99-percent-noble-gas mixtures studied, the corrections in the rate constants for the contributions to the dissociation of Br_2-Br_2 collisions were small. Boundary layer corrections shifted the rate constants to somewhat higher values, the percentage increase being greatest at the lowest temperature. This effect was reflected in decreases in the activation energies of 1 percent for Br_2-Xe and 5 percent for Br_2-He. The activation energies for both systems are well below the dissociation energy of Br_2 (45.5 kcal/mole).

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, May 18, 1970,
129-01.

APPENDIX - SYMBOLS

A	collision partner
B	collision partner
D_0	dissociation energy at 0 K
E_a	activation energy in equation for dissociation rate constant
F	Palmer-Hornig enthalpy correction coefficient
I	transmitted light intensity
I_0	incident light intensity
I_1	transmitted light intensity prior to passage of shock front
I_2	transmitted light intensity following passage of shock front
k_D	dissociation rate constant
$k_{D,M}$	dissociation rate constant resulting from collision with collision partner M
k_R	recombination rate constant
M	collision partner
m	internal degrees of freedom of collision complex
R	gas constant
r	reaction rate
S	optical path length
T	absolute temperature
V_1	velocity of unshocked gas relative to shock front
V_2	velocity of shocked gas relative to shock front
ϵ	extinction coefficient of bromine
τ	laboratory time
[ ]	concentration

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