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The dissociation of Br_2 in Ar was studied in the same shock tube using three different time dependent observables which were needed to measure the rate of the reaction: (1) Br_2 molecular absorption, (2) Br atom two-body emission and (3) density gradient change, detected by laser schlieren technique. It was found that the first observable was most useful in determination of dissociation rate constants between about 1500 and 1800°K and the second observable between about 1200 and 1700°K. Use of these two observables yielded rate constants which were in agreement with those earlier experimental data, which

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In order to interpret the experimental results and to study the dynamics of the reaction, the dissociation of Br_2 in Ar was studied by 3-D classical trajectory calculations at 1500, 2500, 3500, and 6000°K. In agreement with earlier trajectory studies, it was found that Br_2 molecules react only if their total energy is within a few kT of dissociation limit and that metastable molecules, with total energy above the dissociation limit, are particularly reactive. The average energy, $\langle\Delta E\rangle$, and the average angular momentum, $\langle\Delta\ell\rangle$, transferred in dissociative and non-dissociative collisions were calculated as a function of total energy of Br_2 molecule. Generally, $|\langle\Delta E\rangle|$ (non-dissoc.) and $|\langle\Delta\ell\rangle|$ (non-dissoc.) were found to be considerably smaller than the same quantities for dissociative collisions. For energetic metastable molecules, dissociation could be accomplished by a decrease of internal energy and angular momentum of the molecule through collision. Thus, collisionally induced rotational de-excitation provides an additional mechanism for dissociation of diatomic molecules. The non-equilibrium effects in dissociation have been evaluated at 3500 and 6000°K by the method of multiple collisions. The calculated steady state dissociation rate constants between 1500 to 6000°K are in good agreement with the available experimental data.

Finally, the validity of the rate quotient law, i.e. $k_{forward}/k_{reverse} = K_{eq}$, was demonstrated by trajectory calculation technique.

RECOMBINATION OF BROMINE ATOMS BETWEEN 300 AND 6000°K, THEORY AND EXPERIMENT*

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The dissociation of Br_2 in Ar was studied in the same shock tube using three different time dependent observables which were needed to measure the rate of the reaction: (1) Br_2 molecular absorption, (2) Br atom two-body emission and (3) density gradient change, detected by laser schlieren technique. It was found that the first observable was most useful in determination of dissociation rate constants between about 1500 and 1800°K and the second observable between about 1200 and 1700°K. Use of these two observables yielded rate constants which were in agreement with those earlier experimental data, which are likely to be most reliable. The laser schlieren technique yielded new dissociation rate constants between 2100 and 3000°K. These data were found to be consistent with the "reliable" "emission" and "absorption" data, as well as with the earlier flash photolysis data.

In order to interpret the experimental results and to study the dynamics of the reaction, the dissociation of Br_2 in Ar was studied by 3-D classical trajectory calculations at 1500, 2500, 3500, and 6000°K. In agreement with earlier trajectory studies, it was found that Br_2 molecules react only if their total energy is within a few kT of dissociation limit and that metastable molecules, with total energy above the dissociation limit, are particularly reactive. The average energy, $\langle \Delta E \rangle$, and the average angular momentum, $\langle \Delta l \rangle$, transferred in dissociative and non-dissociative collisions were calculated as a function of total energy of Br_2 molecule. Generally, $|\langle \Delta E \rangle|$ (non-dissoc.) and $|\langle \Delta l \rangle|$ (non-dissoc.) were found to be considerably smaller than the same quantities for dissociative collisions. For energetic metastable molecules, dissociation could be accomplished by a decrease of internal energy and angular momentum of the molecule through collision. Thus, collisionally induced rotational de-excitation provides an additional mechanism for dissociation of diatomic molecules. The non-equilibrium effects in dissociation have been evaluated at 3500 and 6000°K by the method of multiple collisions. The calculated steady state dissociation rate constants between 1500 and 6000°K are in good agreement with the available experimental data.

Finally, the validity of the rate quotient law, i.e. $k_{\text{forward}}/k_{\text{reverse}} = K_{\text{eq}}$, was demonstrated by trajectory calculation technique.

1. Introduction

Various earlier investigators have demonstrated that the absolute magnitude of atomic recombination rate constants, k_r, are unusually high, and that they have pronounced negative temperature coefficients. Furthermore, for chlorine, bromine and iodine, k_r, deduced from shock wave dissociation studies, were often found to be
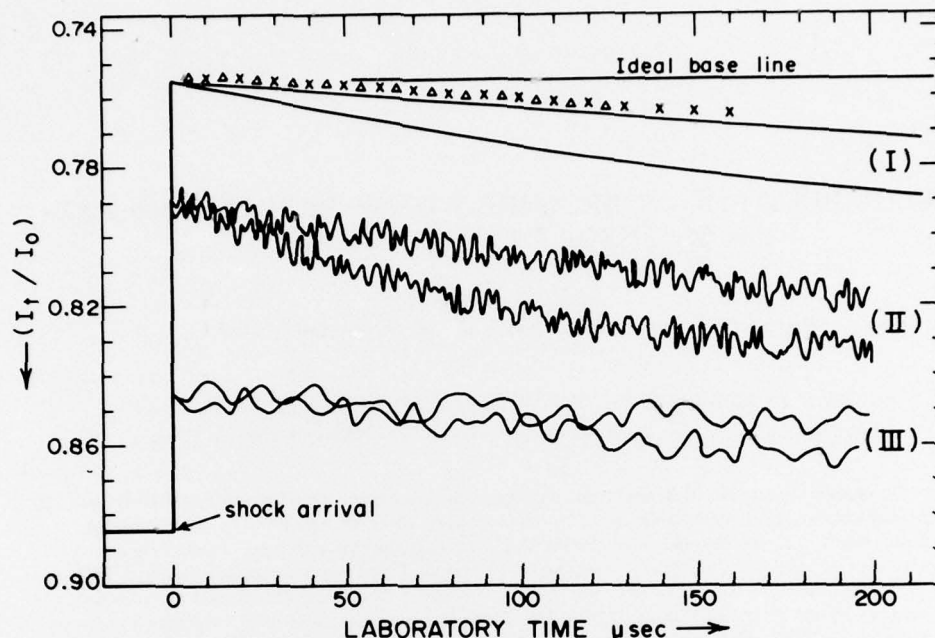
FIG. 1. Experimental shock wave profiles, generated on a computer using rate constants available in the literature. I_0 is the photomultiplier signal before Br_2 is introduced in the shock tube. The initial temperature was 1264°K.

higher than k_r, measured by other techniques, such as flash photolysis which is useful in re-combination rate measurements. These latter findings imply that the rate quotient law, $k(\text{forward})/k(\text{reverse}) = K(\text{eq})$, is violated for the special case of recombination-dissociation reactions. Such experimental data are particularly abundant[1-12] for the case of bromine reacting in an excess of an inert gas.

The purpose of the present investigation was to study the dissociation of bromine in argon in order to

(1) extend dissociation rate measurements over a wider temperature range using shock waves,

(2) interpret the experimental findings in terms of classical trajectory calculations and

(3) uncover possible causes for the above discrepancies.

2. Shock Wave Study of Br_2 Dissociation Rate in Ar

The discrepancies among various shock wave[1,3,5,7] and flash photolysis[10] data for Br_2

$+Ar = 2Br+Ar$ reaction are particularly pro-nounced in the neighbourhood of 1200°K. In order to better understand the nature of the discrepancies, we have generated on the computer the shock wave profiles at 1264°K, using the experimental conditions given in Table III, experiment #8, ref. 7. Details of such com-putations were discussed previously.[1,2] The experimental observable chosen in these com-putations was the optical absorption, I_t, and its time dependence during the reaction. (Optical absorption was the commonly used observable in many experiments.)[3-7]

In Fig. 1, the curve set I, upper line, represents the ideal base line, i.e. no reaction. The middle curve is calculated using the rate constant obtained from flash photolysis experiments[10] and ideal shock wave equations. The lower curve, set I, is derived on the same assumptions, except that the rate constant reported by Warshay[7] is used. Crosses would have yielded the middle curve, except that they were obtained by including the boundary layer effects.[2] Cal-culations described by open triangles are the same as those described by crosses, except that shock attenuation of one percent per meter is assumed. The latter two sets of data indicate

that the discrepancy between the middle and the lower curves cannot be attributed to boundary layer effects and to the shock attenuation.

Curve set II on Fig. I is the same as the middle and lower curves, set I, except that 0.5% shot noise[7] in (I_t/I_0) is assumed. Curve set III is the same as curve set II, except that the time scale is twice as fast as in set II. In order to present the results on the same graph, curves II and III were arbitrarily displaced from the origin, which actually is the origin of curve set I.

A comparison of the two curves, set II, Fig. 1, suggests that it should have been possible to detect a change in rate by a factor of three, which is the discrepancy between shock wave[3,7] and flash photolysis[10] data, especially if the long time records were to be examined. However, it can be also seen from Fig. 1 that slopes from which the rate constants had to be calculated in the experiments[3,7] were small. The base line in such experiments could be ill-defined because of possible imperfections in flow behind the shock front. The existence of random shot noise[3,7] should introduce further uncertainty in rate measurements. For these reasons, the "absorption" shock wave data appear to be relatively unreliable around 1200°K. Such arguments are not valid if slopes of the absorption profiles are appreciable and can be measured unambiguously. The latter situation arises at higher temperatures (1500 to 1800°K), and it is in this range that the rate constants, obtained in absorption spectroscopy experiments[3,5,7] are in a fair agreement with each other and are consistent with flash photolysis data.[10]

If the observable, used for determination of rate constants in shock wave, is the two-body emission,[1,2] then the base line, which corresponds to zero emission, is practically noiseless and is unambiguously defined in experiments. Furthermore, in this case, the shock front position is easily determinable. Therefore, the uncertainty in the rate is largely determined by the noise in the signal itself, provided, of course, that the rate is not too slow or too fast. For these reasons, the two-body emission technique[1,2] should provide accurate rate constants at lowest temperatures. In order to determine the advantages and limitations of this "emission" technique, we have generated on the computer, profiles similar to that shown on Fig. 1, except that we were using the two-body emission as an observable. These profiles suggest that the two-body emission technique is indeed reliable at lowest temperatures, i.e. at about 1200°K, provided that shot noise is not too large. However, it proved to be difficult to define unequivocally the initial rates at highest temperatures, because

the emission is the quadratic function of Br atom concentration. Therefore, the most reliable region for rate measurements using two-body emission technique appears to be between approximately 1200 and 1700°K.

Although the temperature range for reliable measurements, both by "absorption" and "emission" techniques, might have been augmented by use of an improved apparatus, by a larger shock tube, and by varying Br-diluent ratio and Br_2 concentration, it proved difficult in the past to obtain reliable rates of dissociation below 1200°K and above about 2000°K.

It is important to note that the "reliable" shock wave "emission" and "absorption" measurements are in a good agreement with flash photolysis data.[2,9] In order to confirm these conclusions, we have repeated both the "emission" and the "absorption" measurements below 1800°K, using the shock tube, described previously.[1] As anticipated, the results, not shown here, agreed with work of previous investigators.

Under these circumstances, it seemed appropriate to extend the temperature range, employing the same shock tube[1] but using a new laser schlieren[13] detection technique. It was felt that such an approach could better define the dissociation-recombination rate constant over a wide temperature range, and would make a comparison between shock wave and flash photolysis data more meaningful.

In laser schlieren technique, the post-shock density gradient caused by the dissociation is followed by measuring the deflection of a laser beam as a function of time. In order to conduct a laser schlieren experiment, the shock tube, described previously,[1] was fitted with a polished nickel-plated steel pipe one meter long and three inches I.D., and a stable He-Ne CW laser was used to measure the rate. The experimental set-up was similar to that of the previous workers[13–15] and will not be described here. In order to obtain rate constants at highest temperatures, a dilute (3.7%) solution of Br_2 in Ar was used. The rate constants, deduced from the raw data in a conventional manner,[14,15] are shown in Fig. 2.

It can be seen that the combination of "reliable" "emission" data[1] between 1200 and 1700°K, "reliable" "absorption" data between 1500 and 1800°K and new laser schlieren data between 2100 and 3000°K yields a smooth line which is consistent with earlier flash photolysis data.[10] It can also be seen (Fig. 2) that the present results suggest that, at shock wave temperatures, the negative temperature coefficient for the $2Br+Ar \rightleftharpoons Br_2+Ar$ reaction is nearly unity, which is smaller than that reported by previous
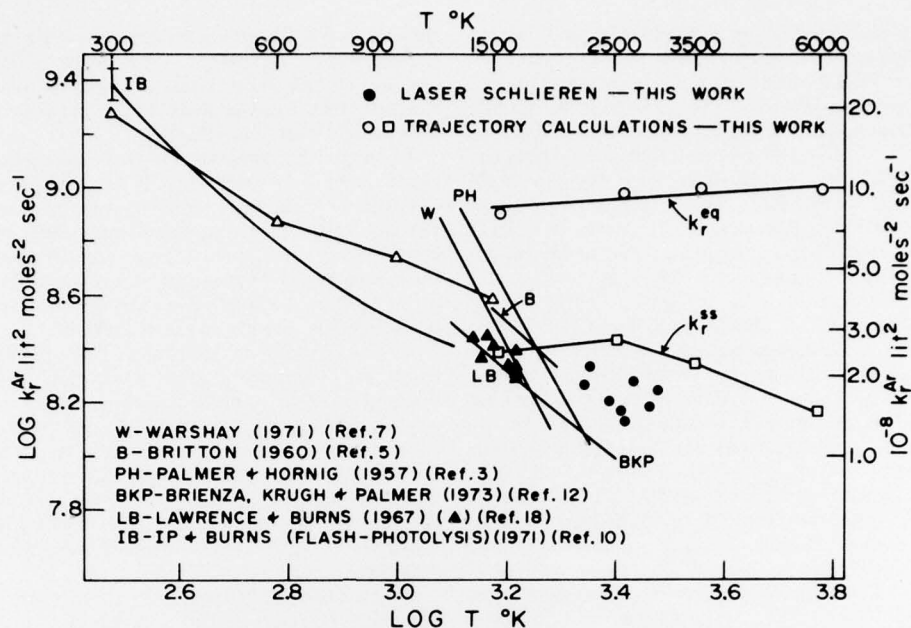
FIG. 2. A comparison of calculated and experimental recombination rate constants for $Br_2 + Ar = 2Br + Ar$ reaction. Ref. 1a presents some additional twenty rate constants, obtained by two-body emission technique below 1700°K, which are in agreement with *LB* data. Open triangles—trajectory calculations of recombination rate constants (Ref. 20).

investigators,[3,5,7] who suggested that the negative temperature coefficient is of the order of three.[16]

3. Dynamics of Dissociation Using Classical Trajectory Method

3-D classical trajectory study of Br atom recombination in argon have already provided useful information on the dynamics and rate constants of the reaction.[17-20] The same principles,[17-20] coupled with stratified and importance sampling techniques[21,22] which improve the statistics of calculations, are used here to study the dynamics of Br_2 dissociation in Ar.

In general, the dissociation rate coefficient at any time t can be written as

$$k_d = (8kT/\pi\mu)^{1/2} \int_R \phi(u) S(u) du \qquad (1)$$

where $S(u)$ is the reaction cross-section, which

is a function of total internal, i.e. vibrational plus rotational, energy u. Here u is averaged over the relative translational energy at temperature T, and ϕ is the normalized distribution function of the reagent, i.e. Br_2, internal energy:

$$\int_R \phi(u) du = 1$$

In the eq. (1) the integration is performed over the entire internal energy space R, compatible with a classically bound molecule. It is known from earlier studies,[17] that the reagent molecules are reactive only if u exceeds a certain minimum value. Therefore, the eq. (1) may be rewritten as

$$k_d = (8kT/\pi\mu)^{1/2} \int_D \phi(u) S(u) \, du \qquad (2)$$

where the subscript D indicates that the integration is executed over the entire reactive energy range. In order to calculate the rate coefficient by sampling only from the reactive
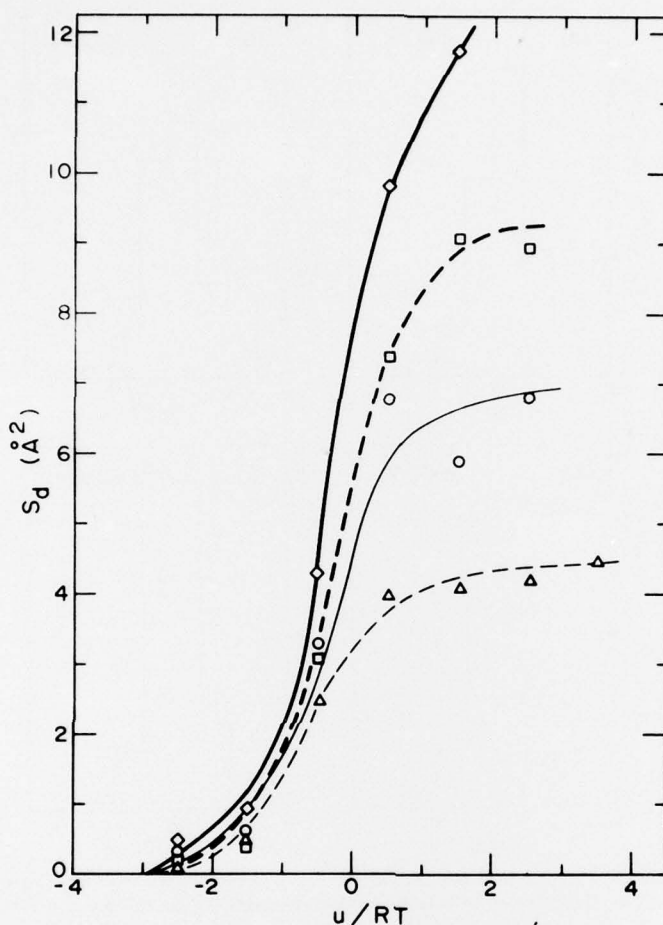
FIG. 3. Dissociation cross-section of Br_2 in Ar, S_d, as a function of Br_2 internal energy. Dashed lines with triangles, 1500°K; solid line with circles, 2500°K; dashed line with squares, 3500°K; solid line with diamonds, 6000°K.

energy range, the eq. (2) may be replaced by

$$k_d = (8kT/\pi\mu)^{1/2} \cdot \left(\int_D \phi(u) S(u) \, du \middle/ \int_D \phi(u) \, du \right)$$

$$\cdot \int_D \phi(u) \, du$$

$$= \langle v \rangle \cdot \langle S \rangle \cdot \int_D \phi(u) \, du \tag{3}$$

where $\langle v \rangle$ is the average relative velocity and $\langle S \rangle$ is the average dissociation cross-section within the entire reactive energy region.

In the subsequent three sections, the dynamical properties of the RHS, eq. (3), are investigated by trajectory method. In Section 7, the dissociation rate constants, calculated from the eq. (3), are compared with the experimental results.

The interaction potential for the system Ar–Br–Br is identical to that used earlier.[20] The well depth and inter-nuclear separation describing the Ar–Br interaction,[20] i.e. ϵ_∞^{ArBr} and σ_∞^{ArBr}, were taken to be 0.5 Kcal/mole and 3.32 Å, respectively. Five strata, 1 kT each, between −3 kT and +2 kT around the dissociation limit, were used.
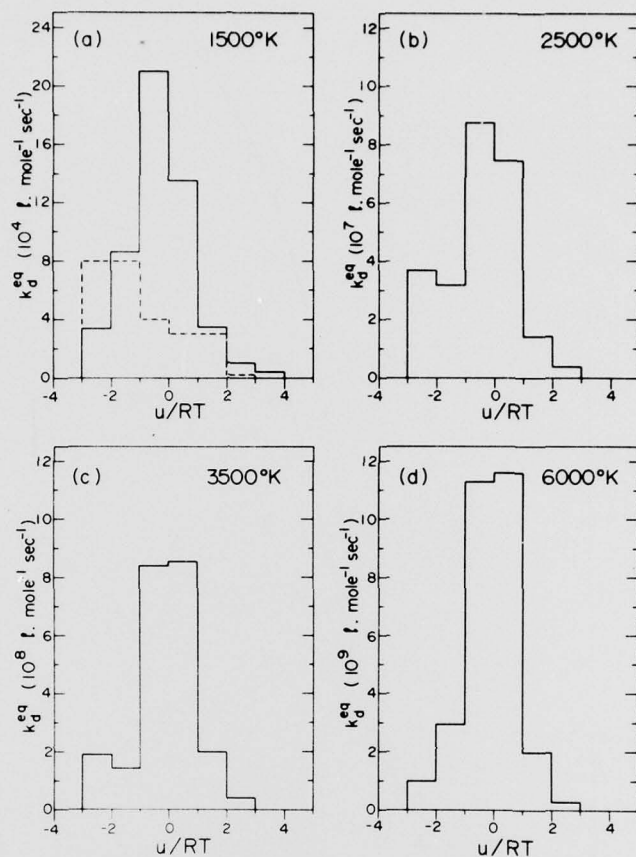
FIG. 4. Contribution to k_d^{eq} as a function of internal energy of the reagent molecule. Note that in 4 (a) the histogram labelled CR, enlarged by a factor of 5, corresponds to the collisional release mechanism.

4. Effect of Br_2 Internal Energy on Dissociation

The dissociation cross-sections of Br_2 in Ar, S_d, are shown in Fig. 3 at different internal energy strata and at four different temperatures. The curves show that only the molecules close to the dissociation limit have an appreciable dissociation cross-section. This finding is in agreement with previous study,[17] which indicates that nascent molecules, formed in recombination, possess energies close to dissociation. There is a large increase of cross-section, as the internal energy of Br_2 increases from bound ($u<0$) to metastable[17] ($u>0$) energy region. The effect is especially pronounced at high temperature. This occurs because metastable molecules have a higher spatial extension, and because they dissociate via the rotational de-excitation mechanism, to be discussed in section 5.

The contribution to k_d^{eq}, the equilibrium rate coefficient[23] (one way flux), from various internal energy strata at different temperatures is shown in Fig. 4. The k_d^{eq} may be defined by eq. (3), using the assumption that the integral $\int \phi(u)\,du$ can be calculated from the Boltzman distribution function and that $\langle S \rangle \equiv \langle S_{eq} \rangle$. At each temperature, the reagent molecules with internal energy less than 3kT below the dissociation limit did not contribute to the rate. Rather, the bulk of dissociation involved molecules within $\pm 1kT$ of the dissociation limit. This result justifies use of eq. (2), rather than equation (1), in our calculations. It also can be seen from Fig. 4 that the metastable Br_2 molecules are just as important as the bound Br_2 molecules in the dissociation processes. Therefore, one may conclude from the principle of detailed balancing, that the nascent products of recombination predominantly popu-
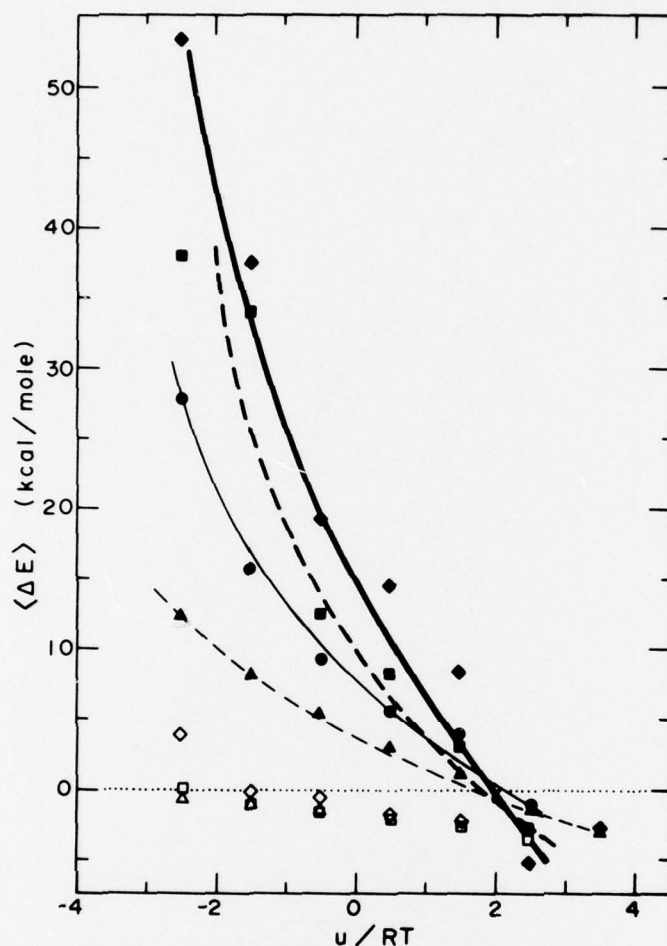
FIG. 5. Average energy transfer *vs.* reagent internal energy. Dissociative collisions are described by filled symbols: heavy solid line with diamonds, 6000°K; heavy dashes with squares, 3500°K; fine solid line with circles, 2500°K; fine dashes with triangles, 1500°K. Non-dissociative collisions are described by the corresponding unfilled symbols, with no lines connecting them.

late the highly energetic states, of which a substantial fraction are the metastable states. This conclusion is consistent with the results of previous recombination studies.[17–19,24–26] At the same time, this conclusion casts doubt on those trajectory calculations[27] which are based on the assumption that deactivation of metastable molecules determines the rate of recombination.

In the present calculations, the collisional release (CR) mechanism of dissociation, defined by $Ar + Br_2 \rightarrow ArBr + Br$, contributes to overall dissociation only at 1500°K. The absence of the CR mechanism at a higher temperature is certainly due to the weak attraction between argon

and bromine atoms. The complete collisional dissociation (CCD) mechanism, defined by $Ar + Br_2 \rightarrow Ar + 2Br$, predominates at all temperatures.

5. Energy and Angular Momentum Transfers in Collisions

The average energy, transferred per collision, $\langle \Delta E \rangle$, is shown in Fig. 5 as a function of Br_2 internal energy. In a reactive collision with a bound molecule, $\langle \Delta E \rangle$ (reactive), is positive. Furthermore, $\langle \Delta E \rangle$ (reactive) is significantly
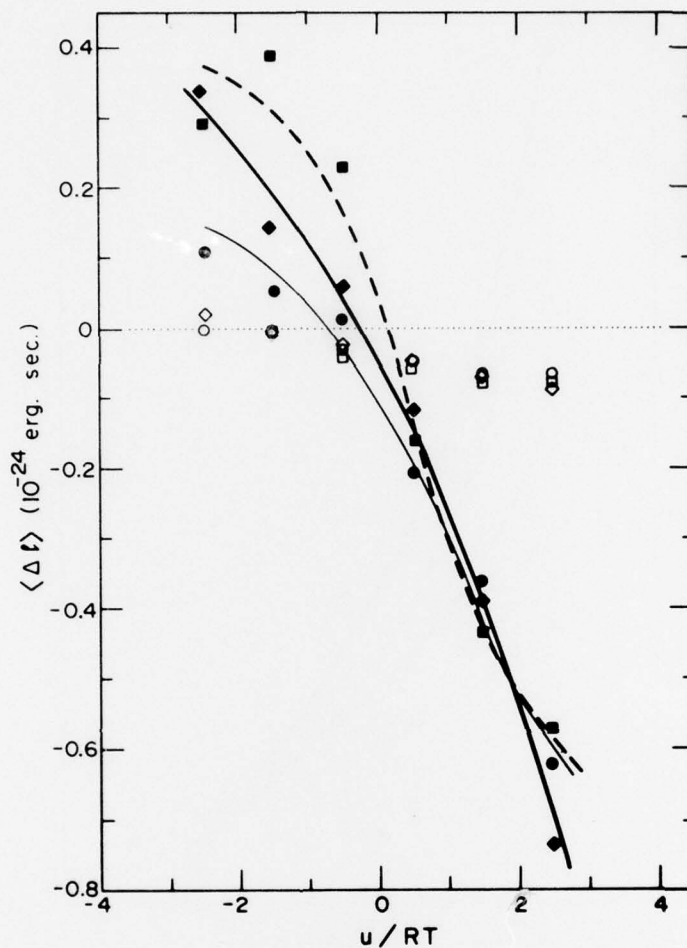
Fig. 6. Average angular momentum transfer *vs.* reagent internal energy. For notations, see captions, Fig. 5.

larger than the minimum amount of energy necessary to excite the molecule just up to the dissociation limit. However, if the diatomic molecule is in a highly metastable state, $\langle\Delta E\rangle$ (reactive) is negative. Since de-excitation of the vibrational motion alone cannot dissociate a classically stable molecule, the dissociation involves loss of rotational energy, which leads to the lowering of the rotational barrier.

In order to study further the angular momentum transfer in energized Br_2 molecules, we defined the average angular momentum transferred in dissociative collisions as

$$\langle\Delta l\rangle_d = \sum_i (l_i' - l_i^0)\omega_i\delta_i^d / \sum_i \omega_i\delta_i^d$$

in which l_i' is the orbital angular momentum of the dissociated pair after collision, l_i^0 is the

rotational angular momentum of the initial diatom, ω_i is the appropriate weight of the ith trajectory, and δ_i^d is a delta function, which is unity if the trajectory is dissociative and zero if otherwise. The average angular momentum transfer in non-dissociative collisions is analogously defined; i.e.

$$\langle\Delta l\rangle_{nd} = \sum_i (l_i^f - l_i^0)\omega_i\delta_i^{nd} / \sum_i \omega_i\delta_i^{nd}$$

where l_i^f is the rotational angular momentum of the diatom after a non-dissociative collision. Thus defined, $\langle\Delta l\rangle$ is positive if there is an increase of angular momentum.

The values of $\langle\Delta l\rangle$ for dissociative as well as non-dissociative collisions were plotted against the Br_2 internal energy (Fig. 6). For the bound states $\langle\Delta l\rangle_d$ was positive, indicating rotational excitation during the dissociation. For metastable
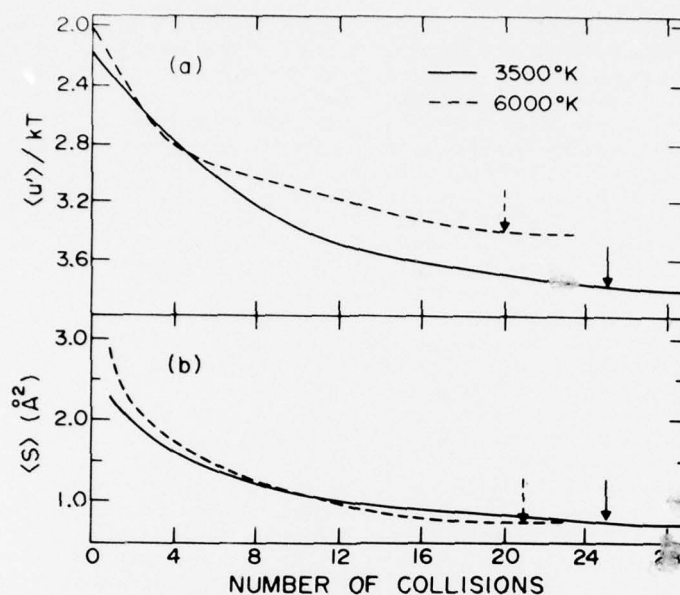
FIG. 7. (a) Evolution of $\langle u' \rangle$ the average internal energy in the reactive energy range. (b) Evolution of the reactivity, as measured by $\langle S \rangle$, the dissociative cross-section in the reactive energy range. For 6000°K, the abscissa is contracted by a factor of two.

species, $\langle \Delta l \rangle_d$ is negative, indicating the lowering of angular momentum during dissociative collisions. This finding corroborates the $\langle \Delta E \rangle$ plots (Fig. 5), and again indicates that rotational de-excitation contributes to the dissociation of metastable molecules. Collisions of metastable molecules with internal energy below $+2kT$, yield negative $\langle \Delta l \rangle_d$ but positive $\langle \Delta E \rangle$ because at this energy, the excitation of vibrational motion outweighs, on the average, the de-excitation of the rotational motion. Figure 6 substantiates an earlier conclusion[24] that vibrational-rotational coupling is strong if molecules, with energy close to the dissociation limit, collide with a third body.

For non-dissociative collisions, Fig. 6 indicates that reagent molecules in highly excited states also experience rotational de-excitation. Furthermore, inelastic collisions yield but a very small $\langle \Delta E \rangle_{nd}$ and $\langle \Delta l \rangle_{nd}$ at all u/RT values, while the corresponding $\langle \Delta E \rangle_d$ and $\langle \Delta l \rangle_d$ are considerably larger (Figs. 5 and 6).

6. Non-Equilibrium Effect in Dissociation

The non-equilibrium effects,[24,28–31] discussed previously,[23,24,28–31] occur because reacting systems, under a steady state condition, cannot be uniquely defined by a Boltzman distribution at temperature T. The non-equilibrium effects may be characterized[24] by the ratio of the rate constant at steady state, i.e. k_d^{ss}, to k_d^{eq} and can be expressed as

$$f = k_d^{ss}/k_d^{eq} = \int_D \phi^{ss}(u) \, du \bigg/ \int_D \phi^{eq}(u) \, du$$
$$\cdot \langle S^{ss} \rangle / \langle S^{eq} \rangle \quad (4)$$

Two factors contribute to the non-equilibrium effect. In the first place, the reactive energy range is depleted by reactive collisions. This factor is determined by the ratio of the integrals of the distribution functions [eq. (4)]. Furthermore, the reactivity in the reactive zone is also decreased; this factor is determined by the ratio of average cross-sections.

Our method of calculation of f factors is based on multiple collision approach,[24] which proved to be successful in earlier trajectory studies on recombination.[18–20,25] The time evolution of the population in the reactive zone can be expressed as

$$\partial N_D/\partial t = -J_d - J_{d \to nd} + J_{nd \to d}$$

in which J_d is the dissociation flux, and $J_{d \to nd}$ and $J_{nd \to d}$ are fluxes representing de-excitation and excitation of molecules from and into the reactive energy range. In the above expression, flux due to recombination of atoms is neglected.

In the present calculation, we generated an equilibrium ensemble of diatomic molecules at temperature T with internal energy within the

reactive zone. We then subjected the initial ensemble to successive collisions with inert gas atoms at the same temperature T. As a result of collisions, a fraction of the ensemble dissociated, and the rest underwent inelastic energy transfer. We assumed that the transfers of molecules in and out of the reactive region resulting from inelastic collisions are identical, i.e. $J_{d \to nd} = J_{nd \to d}$. This assumption implies that the depletion of the reactive zone is solely caused by dissociation, but changes of the energy distribution within the reactive zone are the result of inelastic collisions as well as dissociation. At a steady state, the energy distribution of the ensemble, and its reactivity, are invariant with respect to time and number of collisions. Therefore, the average internal energy, in the reactive zone, $\langle u' \rangle$, and the average dissociation cross-section, $\langle S \rangle$, of the ensemble were chosen as the two parameters in monitoring the establishment of the steady state.

Using this model, we calculated the non-equilibrium effects in dissociation at 3500 and 6000°K. At each temperature an eight hundred trajectory sample per collision was used, but stratified and importance sampling was not attempted. The average internal energy and the average dissociation cross-section in the reactive energy range were studied as a function of the number of collisions. It proved difficult to determine unambiguously at which point the steady state is established. Random fluctuations were pronounced, particularly in $\langle S \rangle$ vs. number of collisions plots. Therefore, the ensemble evolution was studied up to twenty-nine collisions at $T = 3500°$K and up to forty-six collisions at 6000°K. It was possible to obtain relatively smoothly averaged curves (Fig. 7). The non-equilibrium correction was then obtained using equation (4).

7. Comparison with Experimental Data

The calculated equilibrium dissociation rate coefficients yield an excellent linear Arrhenius plot, with an activation energy, ΔE(act), of 44.5 Kcal/mole, assuming that the pre-exponential factor in the rate constant is temperature independent. This number is within one Kcal/mole of the dissociation energy of Br_2 (45.5 Kcal/mole). That the activation energy for k_d^{eq} is approximately equal to the dissociation energy of the diatomic molecule, was also reported by previous investigators.[32]

If the non-equilibrium corrections are made, the computed dissociation rate constants show an appreciable negative curvature in the Arrhenius plot. The curvature is somewhat more pronounced at higher temperatures. The average slope for such a plot yields ΔE(act) = 40 kcal/mole.

In order to compare the present calculations with the results obtained by flash photolysis[10] and shock wave techniques,[1,3,5,7,12] we converted the dissociation rate constants into recombination rate constants using appropriate equilibrium constants (Fig. 2). Since the non-equilibrium correction factors were calculated only at 3500 and 6000°K, it was necessary to estimate these factors at 1500 and 2500°K by extrapolation between 3500°K and lower temperature data.[20] Such extrapolation proved to be unambigious.

It follows from Fig. 2 that the equilibrium recombination rate coefficients yield a positive temperature dependence. After non-equilibrium effects were included in calculations, the recombination rate constants obtained in the present calculations were found to be consistent with flash photolysis data.[10]

Since the calculations of non-equilibrium correction factors were done only at two temperatures, it is difficult to estimate the precision of the calculated rate constants. It is probable, however, that the rate constants are reproducible, approximately within a factor of two. For this reason, the rate constants, obtained in all "reliable" shock wave experiments, are also consistent with calculated dissociation and recombination data.

Finally, it may be pointed out that the agreement between trajectory calculations in recombination domain (open triangles) with the trajectory calculations in the dissociation domain (open squares), demonstrates well the validity of the rate quotient law $[k(\text{forward})/k(\text{reverse}) = K(\text{eq})]$ under the steady state condition (Fig. 2).

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COMMENTS

W. Forst, Université Laval, Canada. I wonder if rate constants measured in various shock tube and flash photolysis experiments are really true *steady-state* rate constants. Could it be that the discrepancy among the experimental data of various investigators, alluded to in your paper, is due to measurements done at various stages of the initial transient that precedes the establishment of the steady-state?

Authors' Reply. In order to measure rate constants in flash photolysis experiments, the concentration of diatomic molecules is followed over a relatively long time. In these experiments, the rate coefficient is always a time-independent rate constant. Therefore, there seems to be no reason to suspect that in these experiments the steady state is not reached. On the other hand, the rate of dissociation of diatomic molecules is often determined from the initial slope in shock tube experiments. This slope may be determined over a relatively short period of time of a few micro-seconds. It may well be that the discrepancy between some shock wave data and flash photolysis data is due to the inability of a shock wave experimentalist to measure true steady-state rate constants. Detailed calculations[1] demonstrate that such a supposition would indeed reconcile some shock wave and flash photolysis data.

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Hajime Miyama, Toray Industries, Inc., Japan. Can you expect much more contribution of collisional release if you change 3rd body from Ar to other species, or change reactant from Br_2 to I_2 according to your calculation?

Authors' Reply. The collisional release mechanism is more important if dissociation-recombination reactions occur at lower temperatures and involve stronger interactions between the recombining atom and a third body. If the third body is an inert gas and the temperature is sufficiently high, so that the dissociation reaction is appreciable, the collisional release mechanism is not important. For the case of iodine dissociation this point was demonstrated recently.[1] On the other hand, at room temperature the atomic recombination appears to proceed via a collisional release mechanism, provided that the third body is sufficiently heavy, such as Xe.[2]

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C. P. Quinn, Shell Research Ltd., England. Does your laser schlieren technique allow you to isolate an incubation period for bromine dissociation and if so how does it compare with the vibrational relaxation time?

Authors' Reply. We were not able to detect an incubation time for Br_2 in our experiments.