

Figure 2. Rates of unimolecular and BCl_3 -catalyzed conversion of cyclopropane to propene expected in 1% CP plus 1% BCl_3 at $p \sim 2.5$ atm: (—) unimolecular rate, given by eq 1 (note: this assumes reaction is at the high-pressure limit; actual rates are somewhat lower); (---) bimolecular rate, given by eq 2.

parameters, might come into play at higher temperatures, particularly in the presence of significant concentrations of radicals. We believe this is happening in the case of propene + BCl_3 at $T \geq 1300$ K. Second, minor errors in activation energy values evaluated at lower temperatures can lead to large errors in predicted reaction rates at ef-

fective laser temperatures. For example, Danen¹² irradiated ethanol in the presence of 2-propanol and HBr, and found that dehydration of ethanol dominated both the dehydration of 2-propanol and acid-catalyzed dehydration of either alcohol. However, his energetic analysis was referenced to a study of 2-methyl-2-propanol dehydration which had reported an activation energy 5 kcal lower than the value we believe from a recent shock tube study.¹³ The higher E_a (and therefore A factor) suggest considerably larger rates for unimolecular dehydration of ethanol or 2-propanol at the effective vibrational temperature (1000–2500 K) than those apparently estimated by Danen. Thus, the reported observation that the ethanol dehydration dominated the lower energy 2-propanol dehydration during ethanol irradiation is remarkable, but the suggestion that the acid-catalyzed reaction would have been expected to be predominant is incorrect.

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Reaction of Hydrogen and Bromine behind Reflected Shock Waves¹

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The reaction of equimolar mixtures of hydrogen and bromine diluted by inert gases was studied in the reflected shock zone over a temperature and total density range of 1400–2000 K and 1.5×10^{-6} – 3.3×10^{-6} mol cm^{-3} , respectively. Infrared emission from HBr passing through a narrow interference filter centered at 3.60 μm was recorded during observation periods typically of 500- μs duration. Conversion of the emission intensity traces to concentration–time data revealed nonlinear product growth for the low-temperature runs and near-linear product profiles at the higher temperatures. The individual experimental profiles were matched with the corresponding model calculations which employed a modern set of rate constants for the various elementary reactions comprising the atomic mechanism. The average percent deviation of 62 experiments from the calculated profiles was 5.4%.

Introduction

Professor Bauer has reviewed recently the status of four-center metathesis reactions² paying particular attention to exchange reactions which he^{3–10} and his col-

leagues^{11–16} have studied for a number of years. These investigations employed the single-pulse shock tube technique. The major finding of these reports is that these homogeneous exchange reactions occur via complex mechanisms that do not involve significant atomic con-

(1) (a) paper presented at the 178th National Meeting of the American Chemical Society, Washington, DC, Sept, 1977. (b) Support of this work by the National Science Foundation, Grant CHE-7608529, is gratefully acknowledged.

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tributions to the overall rate. The experimental evidence for this conclusion rests on an inert gas dependence order in the rate law, order dependencies for the reactants which are inconsistent with atomic or one-step molecular mechanisms, and activation energies which are lower than those predicted for atomic mechanisms or calculated for molecular mechanisms.²

A complementary shock tube approach has been used to study several of the exchange systems investigated by the single-pulse shock tube. The work has been carried out in the reflected shock zone by using infrared emission traces of selected species and time-of-flight mass spectrometry.¹⁷⁻³² The technique involved dynamic analysis of key species. One of the major findings was the recording of nonlinear product profiles which are indicative of a complex reaction mechanism. In those exchange reactions that were studied also by the single-pulse shock tube technique, agreement was obtained with the dynamic method. The formulation of an atomic mechanism encountered the same difficulties of explanation experienced by the single-pulse workers with the exception of HBr + D₂,²³ the self-exchange of oxygen at high temperatures,³¹ ¹⁵NO + C¹⁸O and ¹⁵NO + N₂,³² which could be accounted for by using the appropriate atomic mechanisms.

Since much effort has been expended by experimentalists and theoreticians on this challenging problem and, in particular, on the H₂ + D₂ exchange, it is desirable to demonstrate the validity of the shock tube technique on a reaction system for which the mechanism is well-known and which has characteristics that are related to the exchange reactions.

The reaction of hydrogen with bromine meets many of these requirements. The rate constants at high temperatures have been measured and preliminary model calculations revealed a temperature and density range available to our apparatus in which the product profiles would vary from nonlinear to linear depending upon the time required for the establishment of the steady-state approximation for the atoms. A previous shock tube study of this reaction monitored the visible emission from Br₂ at 500 nm. The data were reduced by taking a single point from the time-dependent trace corresponding to 25% disappearance of Br₂.³³

Furthermore, the mechanism for H₂ + Br₂ is known to be dominated by three-center reaction steps and that the contribution of the four-center step, H₂ + Br₂ → 2HBr, is insignificant. Hence, this system offers a marked contrast to those exchange reactions investigated by the shock tube technique and found to be dominated by four-center rather than three-center steps.

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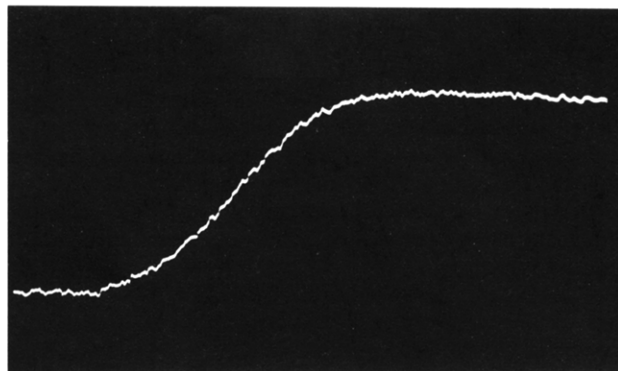


Figure 1. Infrared emission trace from a 3% H₂-3% Br₂ mixture reacting at 1791 K. The sweep speed is 50 μs/cm.

TABLE I: Arrhenius Parameters for Computer Simulation Program^a

reaction	A	E*	ref
1	1.55×10^{-10}	88.9	34
2	$3.47 \times 10^{-12} T^{0.5}$	38.14	35
3	2.32×10^{-10}	19.57	36
4	7.47×10^{-10}	2.98	36
5	2.57×10^{-12}	50.0	37

^a A is given in units of cm³ molecule⁻¹ s⁻¹; E*, kcal mol⁻¹.

Experimental Section

The equipment and procedures employed have been described previously.²⁶ An Infrared Industries 3.60-μm (0.22-μm half-band width) interference filter was selected to monitor the infrared emission signal from HBr. The trace was digitized by a Biomation 610B transient recorder. A total of 255 points was recorded for each experiment during a typical observation time of 500 μs.

Three reacting mixtures were prepared: (A) 0.75% H₂-0.75% Br₂; (B) 1.5% H₂-1.5% Br₂; (C) 3% H₂-3% Br₂. The diluent used for the balance of all mixtures consisted of equimolar amounts of helium and argon. Three calibration mixtures were employed: 1.5% HBr; 3% HBr; 6% HBr; all with He-Ar diluent.

ACS Reagent grade bromine was purchased from Matheson Coleman and Bell. Hydrogen bromide (Matheson, 99.8%) was purified with bulb-to-bulb distillation. Linde hydrogen (99.95%) was condensed onto a molecular sieve at liquid nitrogen temperature. The top portion off the sieve was used. Linde argon and helium (99.5%) were used without further purification.

The calibration mixtures served to construct signal height vs. concentration plots and to check the extrapolation of shock velocity measurements with the observed shock arrival time at the observation port slit. The cleanliness of the shock tube was monitored periodically with runs of pure argon shocked to detect the presence of any emitting species. High-temperature argon shocks were effective in scrubbing the tube of any adsorbed species.

Results and Discussion

Polaroid film was used to record the emission trace shown in Figure 1. Shock arrival time at the observation port slit located 3.2 mm from the end wall was determined by extrapolation of the shock velocity to the slit position. The velocity was measured with four thin film gauges. The last gauge was located 5 cm upstream from the slit.

The digitized data were plotted from each experiment after conversion to HBr concentration expressed in molecules cm⁻³. Mixture A was shocked at initial pressures of 5 and 10 torr. Mixtures B and C were shocked at 5-torr

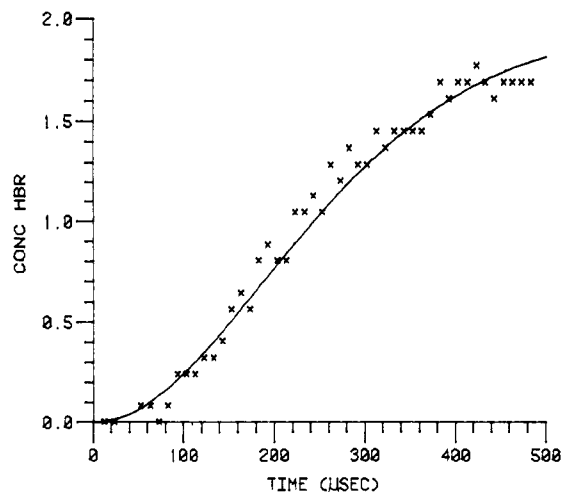
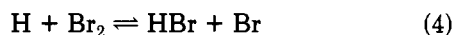
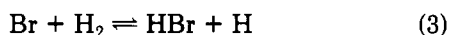
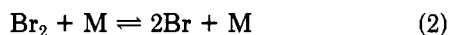


Figure 2. Reaction profile for [HBr] at 1580 K. The solid line represents computer simulation.

starting pressure. A total of 64 calibration runs were performed which covered the entire range of reflected shock density and temperature. The relation between signal height and HBr concentration was found to be linear.

The experimental profiles were compared to calculated profiles constructed from the following reactions:



The rate constants for the mechanism are listed in Table I.

Plots of the data and corresponding model calculation are depicted in Figures 2 and 3. Figure 2 is typical of an experiment in which the steady-state concentration of atoms has not been attained. The product profile is nonlinear. Figure 3 displays a run at higher temperature in which the steady state is achieved early in the observation period and the profile appears to be almost linear.

The experimental data of each run were compared to the calculated profile by using the following relation:³⁸

$$\text{pM} = \log \frac{[\text{HBr}]_{\text{calcd}}}{[\text{HBr}]_{\text{expt}}}$$

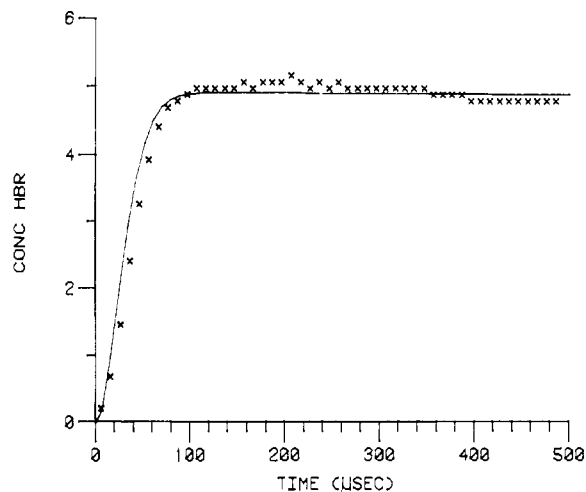


Figure 3. Comparison of experimental data for [HBr] at 1998 K and calculated profile.

The average value for pM for the 62 runs is -0.00232 , the average absolute value is 0.0570, and the average deviation is 5.4%.

This agreement represents additional evidence for the validity of the shock tube technique. Many of the runs reached an equilibrium level which is a check on the reflected zone temperature calculated from the shock velocity measurements. The kinetic portion of the profile is related to the three other shock tube reports from different laboratories.^{34,35,37}

The work described herein does not offer a solution to the exchange reaction mechanism problem, but it does represent an application of modern chemical kinetics to a classic reaction and goes beyond the usual textbook treatment which does not address the H₂ + Br₂ system under non-steady-state condition.

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