[CONTRIBUTION FROM THE JAMES FORRESTAL RESEARCH CENTER, PRINCETON UNIVERSITY]

The Hydrogen–Bromine Reaction at Elevated Temperatures[1]

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The onset of explosions in mixtures of hydrogen and bromine both with and without added inert gases has been studied in the temperature range 850–1140°K. A shock wave compression technique was used in order to heat the mixtures to the explosive range in times short compared to the "induction periods" preceding explosion. The phenomenon can be treated adequately as a thermal explosion. The reaction sequence established for the low temperature hydrogen–bromine reaction and suitably extrapolated values of the individual rate constants suffice for a quantitative explanation of the temperature dependence of the induction times. The usual assumption of "steady state" concentrations of Br and H atoms is not applicable here.

Introduction

The gas phase reaction between hydrogen and bromine is considered a classic example of a process for which the rate is well known and the mechanism firmly established. The basis for this is a large series of experiments on the thermal and photochemical reaction at temperatures below 575°K.[2] The mechanism and the evaluation of the rates by Campbell and Hirschfelder[3] are given in Table I.

TABLE I

MECHANISM AND RATE CONSTANTS FOR HBr PRODUCTION AT LOW TEMPERATURES[2]

$Br_2 + M \rightarrow Br + Br + M$

$k_1^f = 1.439 \times 10^{18}\ T^{1/2} \exp(-46{,}053/RT)$ cc./mole-sec.

$Br + Br + M \rightarrow Br_2 + M$

$k_1^r = 1 \times 10^{16}$ cc.^{2}/mole^2-sec.

$Br + H_2 \rightarrow HBr + H$

$k_2 = 3.46 \times 10^{10}\ T \exp(-16{,}640/RT)$ cc./mole-sec.

$H + Br_2 \rightarrow HBr + H$

$k_3 = 6.423 \times 10^{12}\ T^{1/2} \exp(-1100/RT)$ cc./mole-sec.

$H + HBr \rightarrow H_2 + Br$

$k_4 = 7.65 \times 10^{11}\ T^{1/2} \exp(-1100/RT)$ cc./mole-sec.

$k = 2k_2(k_1^f/k_1^r)^{1/2} = 8.302 \times 10^{11}\ T^{3/4} \exp(-39{,}666/RT)$

$d[HBr]/dt = k[Br_2]^{1/2}[H_2]/(1 + k_4[HBr]/k_3[Br_2]) = 2S$

Because the system is well understood, it has been used as a model for theoretical calculations of flame speeds, with the hope that a correlation between the observed properties and the chemical kinetics could be found. Significant progress has been made, but the correlation between chemical and aerothermodynamic properties has not been so good as had been hoped.[4,5]

The explosion limits of H_2–Br_2 mixtures agree qualitatively with thermal theory[6] and are represented by

$$\log (P/T) = E^*/2.3nRT + \text{Constant}$$

where $E^* = 27.6$ kcal./mole if n, the reaction order, is $^3/_2$ for any given mixture.[7,8] The minimum explosion temperature is 740°K. and occurs for $^1/_3$ H_2–$^2/_3Br_2$. Quantitatively the low "activation energy" and the composition of the mixture with the minimum explosion temperature are inconsistent with the low temperature mechanism.

As a result of the poor correlation, the general question of the applicability of the low temperature kinetic data to high temperature phenomena has been reopened. We report here on a study of the system at temperatures (850–1140°K.) immediately above the explosion limit. Both our results and those of Britton and Davidson[9] at 1400°K. indicate that the elementary steps in the low temperature mechanism and extrapolated values for their rate constants apply at high temperatures.

Experimental

Procedure.—Mixtures of hydrogen and bromine (and inert gas) were heated rapidly to the explosive temperature region by means of a shock compression technique. This method, previously used by Zeldovitch[10] for explosion limit studies, is analogous to the rapid piston compression technique[11] but much faster.

A previously prepared gas mixture was admitted to the evacuated shock tube to a pressure less than one-fifth atmosphere. One end of the tube was closed by a thin cellophane diaphragm. Rupture of the diaphragm initiated a shock wave compression supported by the inrush of air from the room. Near the closed end of the tube were located two photometers for determining the optical density of the bromine in the gas mixture. As the leading edge of the shock wave reached the first photometer, the sudden change in bromine density caused a change in the output of a photomultiplier tube. This drove a single horizontal sweep on an oscilloscope. At the same time, the output of the second photometer was displayed on the vertical scale of the oscilloscope. The resulting transient (photographed for later analysis) represented the history of the bromine optical density and thus the concentration at the level of the second phototube during the course of the

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[2] See, for example, R. N. Pease, "Equilibrium and Kinetics of Gas Reactions," Princeton University Press, Princeton, N. J., 1942.

[3] E. S. Campbell and J. O. Hirschfelder, University of Wisconsin Report CF-2108, NORD 9938.

[4] D. F. Mileson, California Institute Technology, Technical Report No. 6 (1954) "The Thermal Theory of Laminar Flame Propagation for Hydrogen–Bromine Mixtures."

[5] E. S. Campbell, University of Wisconsin, Report CM 849, NORD 15884 "Integration of a Simplified Kinetic Model for a Hydrogen–Bromine Flame."

[6] N. Semenoff, "Chemical Kinetics and Chain Reactions," Oxford, 1935, p. 79 ff.

[7] A. B. Sagulin, *Z. physik. Chem.*, **B1**, 275 (1928).

[8] V. Kokochashvili, *Zhur. Fiz. Khim.*, **23**, 15, 21 (1949); **24**, 268 (1950).

[9] D. Britton and N. Davidson, *J. Chem. Phys.*, **23**, 2461 (1955).

[10] I. T. Gershanik, I. A. Zeldovitch and A. I. Rozlovski, *Zhur. Fiz. Khim.*, (*USSR*), **24**, 85 (1950). We are indebted to Professor G. B. Kistiakowsky for suggesting the possible use of this method for kinetic studies.

[11] E. S. Taylor, C. F. Taylor, W. Leary and J. Jovellanos, NACA T.N. 1332 (1948), "Rapid Compression Machine Suitable for Studying Short Ignition Delays."

experiment. The duration of most experiments was two to seven milliseconds. After the end of the experiment, the diaphragm fragments were removed, the shock tube reassembled and evacuated. No other precautions were taken to eliminate traces of foreign gases, nor was any special treatment of the tube walls needed in order to assure reproducibility.

Reagents.—Merck N. F. bromine was distilled through KBr and stored in an ampule sealed onto the glass reaction system. Hydrogen and helium (American Oxygen Service Co.) and argon (Matheson) were used without purification. Mixtures of gases were made up by admitting first bromine and then the permanent gases to large glass reservoirs. At least 12 hours mixing time was allowed before use.

Apparatus (Fig. 1).—The shock tube, Pyrex glass, 120 cm. long and 2.1 cm. inside diameter, was sealed flat at one end. The other end was closed by the cellophane diaphragm (5×10^{-4} inch thick) held in a stainless steel holder which, in turn, was fitted onto the glass tube. Rubber "O" rings provided the necessary vacuum tight seals between the diaphragm and holder and between the holder and tube. The lower 110 cm. of the shock tube was heated electrically to 110–117° by "Briskeat" tapes wrapped around the air jacket. The bottom 30 cm., which included all measuring stations, was kept at 117 ± 1°. This was used as the initial temperature in all calculations.

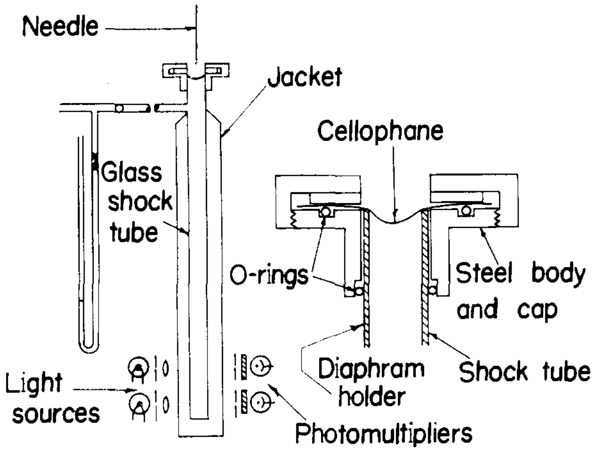

Fig. 1.—Shock compression equipment.

The two optical arrangements used to feed the oscilloscope were identical. In each, collimated white light (a thin sheet perpendicular to the axis of the tube) passed through the jacket and reaction tube and through a second collimating slit, then was filtered to permit only a band from 410 to 420 mμ to pass (Corning optical filters Nos. 5113 and 3389 in series) and finally fed to a 931A type photomultiplier tube.

Both photomultipliers were powered by the same adjustable high-voltage power supply. Their outputs were monitored with microammeters thus permitting rapid adjustment of the optical system and calibration of the oscillographic records. The output of each tube was fed through a "cathode follower" circuit to the oscilloscope (Dumont Model 248). The phototube closer to the open end of the shock tube that served to "trigger" the 'scope responded to the change in bromine density. Though much less sensitive than the Schlieren technique used by Davidson,[12] it was easy to adjust and maintain.

The output of the other phototube was amplified (vertical d.c. amplifier of a Hickok Model 640 oscilloscope) and then fed directly to the vertical deflection plates of the picture tube of the Dumont 'scope.

The long duration of the experiments necessitated modification of the 'scope circuits to include an 0.01 second sweep. Time intervals were established by means of an Owen Laboratory Type 160 Oscilloscope Time Calibrator. In some studies in which only shock speeds were measured, the phototubes were connected directly to a Potter Instrument Co. Model 850F Electronic counter.

Results

Description of the Compression Process.—Oscillograms, particularly those obtained in order to study the speed of compression, showed that this process was a series of shock waves. The speeds of these shocks and observed bromine density changes across them were qualitatively consistent with the predictions of shock tube theory.[13–16] An idealized pictogram of the wave compression process that probably occurs is shown in Fig. 2. A tracing of an oscillogram of the bromine density is shown in Fig. 3. In terms of Fig. 2,

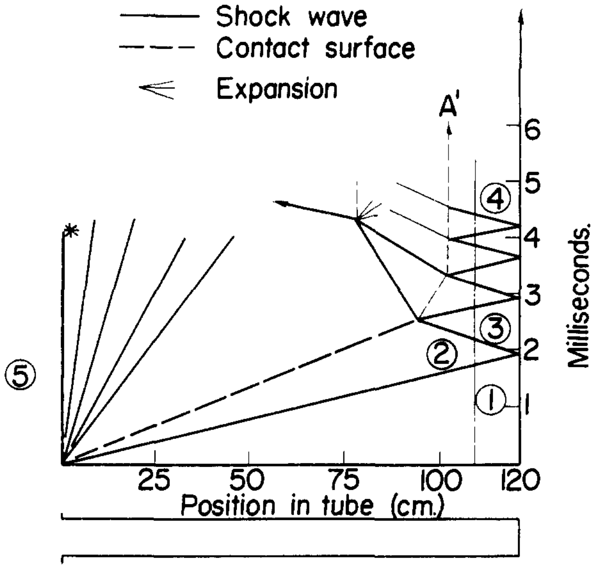

Fig. 2.—Shock wave diagram for open ended tube: P_1 = 0.1 atm., T_1 = 390°K., P_5 = 1 atm., T_5 = 300°K., $\gamma_1 = \gamma_5$ = 1.4; * indicates sonic velocity at mouth of tube; non-isentropic inflow (Borda nozzle) assumed.

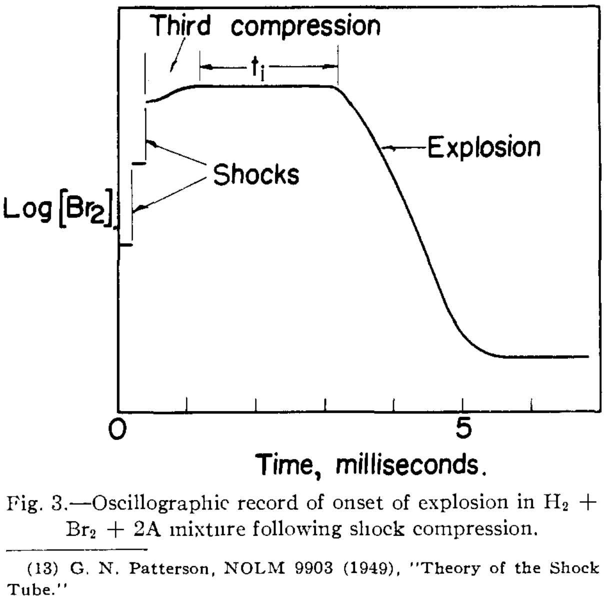

Fig. 3.—Oscillographic record of onset of explosion in H_2 + Br_2 + 2A mixture following shock compression.

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[12] T. Carrington and N. Davidson, *J. Chem. Phys.*, **57**, 418 (1953); D. Britton, N. Davidson and G. Schott, *Disc. Faraday Soc.*, **17**, 58 (1954).

[13] G. N. Patterson, NOLM 9903 (1949), "Theory of the Shock Tube."

[14] R. Courant and K. O. Friedrichs, "Supersonic Flow and Shock Waves," Interscience Publishers, New York, N. Y., 1948, pp. 152–4.

[15] G. Rudinger, "Waves Diagrams for Non-steady Flow in Ducts," D. Van Nostrand, New York, N. Y., 1955.

[16] J. Lukasiewicz, NRC Report MT-11(1950), "Flow in a Shock Tube of Non-uniform Cross Section."

the oscillogram corresponds to an observation taken at the position indicated by a vertical dot-dash line. The incident shock between regions 1 and 2 and the reflected shock between 2 and 3 are evident. We did not observe the additional shocks that should follow interaction of the reflected shock with the contact surface between the reactive mixture and the "piston" gas. Invariably this appeared as a gradual compression. Accordingly, we have treated it as adiabatic.

The process studied here differs in two ways from other applications of shock tubes to the study of chemical reactions.[9,12,17] Normally, the reaction occurring in the heated, compressed gas in region 2 is studied. We consider the fate of the mixture following the complete compression (A′). Fortunately, it is the last stage that raises the gas temperature to the explosive region.

The normal shock tube has a finite length high pressure (piston) section with the same cross section as the low pressure (reaction) part. The piston section of our tube was "infinitely" long and wide, namely, the laboratory. Lukasiewicz[16] analyzed the behavior of this type of tube and concluded that appreciably stronger (*ca.* 15–20%) shocks should be formed than those in normal shock tubes at the same diaphragm pressure ratio. In consequence, the over-all temperature and pressure rises are greater, and the apparent anomaly of the reaction gas being compressed to a pressure higher than that originally in the piston section can occur. We have observed shock speeds in excess of those predicted by normal shock tube theory and have found densities corresponding to super-atmospheric pressures. These were shown to be real and not a fiction of the experimental measurements by means of experiments with a 36 cm. long high pressure section of the same diameter as the shock tube. The experiments with the normal diameter piston section showed the attenuation that is expected in a narrow normal shock tube. In a similar manner, the results obtained with the "infinitely wide" piston section were lower than those Lukasiewicz predicted assuming isentropic flow into the tube. Surprisingly enough, the observed velocities were comparable to those that correspond to non-isentropic (Borda nozzle) inflow.[15] The data on this point are recorded elsewhere.[1]

A steady shock velocity was not observed. Instead, the average speed measured over an 11 cm. path near the closed (bottom) end of the tube was slightly higher than the average speed for the bottom 26 cm. The cause of this is unknown but it is not due to reaction, since it also occurred in a mixture of 5% bromine in air. In all cases the velocities measured near the end of the tube were used in temperature and pressure calculations.

Determination of the State of the Compressed Gas.—Since neither normal shock theory nor the "infinitely wide" piston theory may serve to determine the temperature rises in our experiments, an empirical correlation of shock velocities and diaphragm pressure ratios was made. Measurements on 5% bromine in air (referred to above) showed that the ratio of observed velocity to normal shock tube velocity was 1.104 ± 0.015 over the diaphragm pressure ratios employed in the other experiments. Less reliable measurements on hydrogen containing mixtures gave ratios of 1.118 ± 0.04 for $3H_2 + Br_2$ and 1.13 ± 0.03 for $H_2 + Br_2 + 2A$. (In each case the standard deviation is given.) For convenience, and as a conservative estimate of the departure from normal shock theory, the ratio 1.10 has been used in the calculations based upon the equations below. (The particular method of calculation, seemingly round about, was expedient because normal shock tube velocity–diaphragm ratio correlations were already available).

Shock velocities were calculated from diaphragm pressure ratios using normal shock tube theory[13] (notation as in Fig. 2)

$$\frac{P_1}{P_5} = \frac{P_1}{P_2}\left[1 - \left(\frac{P_2}{P_1} - 1\right)\sqrt{\frac{\beta_5 E}{1 + \alpha_1 P_2/P_1}}\right]^{\frac{1}{\beta_5}}$$

$$w = a_1\sqrt{\beta_1\,(1 + \alpha_1\,P_2/P_1)} \quad (1)$$

where

$\beta = (\gamma - 1)/2\gamma,\ \alpha = (\gamma + 1)(\gamma - 1),\ E = \beta_5/\beta_1\,(a_1\gamma_5/a_5\gamma_1)^2$

γ is the specific heat ratio, a the speed of sound and w the shock velocity. The value of w was increased by 10%, P_2/P_1 recalculated and then the temperature rise across the first shock obtained

$$\frac{T_2}{T_1} = \frac{(P_2/P_1)(\alpha_1 + P_2/P_1)}{1 + \alpha_1(P_2/P_1)} \quad (2)$$

The conditions after passage of the reflected shock are uniquely determined by the first wave.[13] The pressure jump is given by

$$\frac{P_3}{P_2} = \frac{(2 + \alpha_1)(P_2/P_1) - 1}{(\alpha_1 + P_2/P_1)} \quad (3)$$

and the temperature ratio by an expression identical in form to eq. 2. Any additional compression was treated as adiabatic and its magnitude was based on the oscillographic records of the bromine density change across it

$$T_4/T_3 = (\rho_4/\rho_3)^{\gamma_1 - 1},\ P_4/P_3 = (\rho_4/\rho_3)^{\gamma_1} \quad (4)$$

This stage represented, at most, 20% of the heating process. Where practical, density ratios across the shock waves were checked against those calculated from velocities. Agreement was reasonable.

The Mixture after Compression.—In a nonreactive mixture the density of bromine remained nearly constant in the period following compression, until the arrival of an expansion wave from the open end of the tube ended the experiment. A small drift toward higher densities was noted, and was analyzed on the assumption that it represented cooling in a narrow region near the tube wall. The analysis indicated that the cooling was slight. For example, a mixture of 3 parts He and 1 part Br_2 at 790°K. cooled 24° in 6 milliseconds. Rough estimates of the Prandtl number were also made. These ranged from 1.5 to 3, values consistent with a boundary layer effect, as opposed to those for purely conductive (0.7–0.8) or convective (<0.7) heat transfer. The effect has been ignored in the interpretation of the explosion data.

Mixtures of H_2 and Br_2 (and inerts) showed the same slight cooling when the temperature (T_4) was

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(17) H. S. Glick, W. Squire and A. Hertzberg, "5th Symposium (International) on Combustion," Reinhold Publ. Corp., New York, N. Y., 1955, p. 393.

relatively low. At higher temperatures a constant, or, at times, slowly decreasing bromine density was observed. This state was then terminated by a very rapid extensive decrease in bromine density (Fig. 3). In no case was a regime established in which a steady decrease in bromine density occurred that did not end in such an explosion.

The explosions were studied in six hydrogen–bromine mixtures and the induction periods measured. The data are recorded in Table II. The dependence of the induction periods upon the temperature to which the sample had been heated was determined from plots of log t_i *versus* $1/T_4$.

Such plots showed a linear relationship, within the spread of the data. The "apparent activation energies" for the three mixtures studied most extensively were: 23 kcal./mole ($3H_2 + Br_2$), 27.5 kcal./mole ($H_2 + Br_2 + 2A$) and 24 kcal./mole ($H_2 + Br_2 + 2He$).

The precision and accuracy of the temperature measurements, important considerations in assessing the mean of the activation energies quoted above, are difficult to determine. Two estimates may be given. An error in the measurement of the shock velocity of 1% propagates as such in T_2/T_1, for the shock speeds considered here. If such is the sole source of error in T_4, a precision of about 2% may be assigned to it.

On the other hand, if the data for mixture II are assumed to obey an Arrhenius expression: $\log t_i = A(1/T) + \text{constant}$, and t_i is assumed to be measured without error, the standard error in $1/T$ suggests a precision of about 6%. Since the induction times are valid to only two significant figures, this rough estimate, throwing all error in the temperature measurement, must be considered a maximum.

The accuracy of the temperatures is even more difficult to assess. Due to our low estimate of the departure of the shock tube behavior from normal shock tube theory, the report temperatures may be one to 3% too low. Other uncertainties are undoubtedly greater.

Finally, it may be observed that a systematic error of at least 6% in T, the higher temperatures being too great would be needed to produce apparent activation energies of 36–40 kcal./mole.

Discussion

The results show a feature not previously observed in explosion studies on this system, the existence of measurable time delays prior to explosion. The failure of other workers to note this probably was due to the methods used, which required comparatively lengthy heating periods. The induction periods are similar to the limit studies having about the same temperature dependence, markedly lower than that observed in the low temperature reaction. Thus it is likely that the same phenomenon has been observed in both types of experiment.

Since heat losses seem to be unimportant in our experiments, we have considered an adiabatic thermal explosion as a model for the system, following the approach of Rice.[18]

TABLE II

OBSERVED INDUCTION PERIODS (t_i) OF THERMAL EXPLOSIONS OF $H_2 + Br_2$ MIXTURES AT VARIOUS TEMPERATURES. MIXTURES (I) $3H_2 + Br_2$ (II) $H_2 + Br_2 + 2A$ (III) $H_2 + Br_2 + 2He$ (IV) $3H_2 + Br_2 + 4A$ (V) $H_2 + Br_2 + 6A$ (VI) $3H_2 + Br_2 + 12A$

Mixture	P_5/P_1	P_4, atm.	T_4, °K.	t_i, millisec.
I	12.67	1.238	920	1.9
	10.86	1.253	873	3.5
	19.00	0.811[a]	950[a]	1.3[a]
	15.20	1.217	979	0.8
	15.20	1.217	979	0.8
	19.00	0.811[a]	950[a]	1.2[a]
	12.60	1.238	918	2.0
	10.80	1.254	871	2.8
	14.54	1.221	964	0.8
	9.95	1.264	847	4.5
II	12.58	1.125[a]	1030[a]	0.5[a]
	7.55	1.486	911	2.4
	6.86	1.496	879	4.3
	8.58	1.467	956	1.1
	10.20	1.193[a]	962[a]	1.1[a]
	7.86	1.481	925	1.7
	7.12	1.491	892	3.1
	15.73	1.050[a]	1111[a]	0.5
III	12.60	0.952[a]	954[a]	1.4[a]
	6.87	1.410	851	6.6
	9.45	1.400	961	1.4
	7.71	1.406	889	3.8
	8.59	1.402	927	2.2
	10.80	1.397	1015	1.1
	7.13	1.409	863	5.4
IV	12.34	1.379	1091	0.7
	7.22	1.397	882	6.5
	9.11	1.384	966	1.35
	20.13	0.779[a]	1111[a]	0.6[a]
	19.12	0.796[a]	1095[a]	0.7[a]
V	9.37	1.434	1080	1.0
	7.11	1.468	962	2.2
	8.00	1.459	1008	1.2
	6.40	1.475	921	4.2
	12.67	1.030[a]	1095[a]	0.9[a]
	6.33	1.478	919	4.5
	9.27	1.446	1075	0.5
VI	10.83	1.402	1144	1.25
	12.63	1.411	1226	1.0
	7.58	1.406	981	2.5
	6.32	1.449	910	7.5

[a] T_m, P_m and t_i measured from second shock wave.

Induction periods were calculated for the onset of explosion in mixture II on the basis of several sets of assumptions. The results are summarized below. The pertinent mathematical developments are given in an appendix.

If it is assumed that the rate constant for the hydrogen–bromine reaction is an extrapolation of the low temperature value, and that the steady (equilibrium) state in Br atoms exists, the temperature history of a mixture starting at a given T_4 and P_4 may be obtained by direct integration of eq. 5 to yield (7). An arbitrary criterion for the length of an induction period must be chosen. We have used a rise in temperature of 100° above T_4, at which point the T *vs.* t curve is rising very rapidly. This procedure yields induction periods with a temperature dependence slightly lower than the input value,

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[18] O. K. Rice, A. O. Allen and H. C. Campbell, THIS JOURNAL, **57**, 2212 (1935).

i.e., assuming $E^* = 40.2$ kcal./mole, the "induction period activation energy" was 36.9 kcal./mole for mixtures I, II and III. The curve for mixture II is the dashed line in Fig. 4. When a heat loss term was included in this model, it proved to affect only the induction periods of mixtures close to the explosion limit, and not the rest of the range of interest. This is because the exponential temperature dependence of the reaction rate constant overrides the heat loss.

That the steady state assumption cannot be made for these explosions is demonstrated as follows. It is practical to calculate (to a good approximation) the time required, at constant temperature, for the Br atom concentration to rise from zero to its equilibrium value in the mixtures studied here (Appendix, Section 2). The times involved are shorter than, but within an order of magnitude of the observed induction periods. About two-thirds as much HBr is produced during this non-steady period as during the same time under steady-state conditions. This indicates that an appropriate model for the explosion would be an adiabatic system in which the hydrogen–bromine reaction proceeds from zero atom concentration through the build-up period toward the steady rate. In order to test the adiabatic non-steady model we have integrated eq. 9 graphically with S and A as functions of temperature. This is tantamount to assuming that the rate of buildup of the atom concentrations will have the same functional form in the adiabatic as in the isothermal case. A check numerical integration of the general non-linear set of equations describing the system verified the applicability of the approximate graphical method. The result of the latter for mixture II is shown as a heavy line in Fig 4.

The best fit of the data was obtained using the value of k given in the appendix and a choice of $k_1^r = 10^{15}$ (cc./mole)^2 sec.$^{-1}$. The latter choice affects k_1 through the equilibrium constant and controls A in eq. 9. The value is lower than that given by Campbell but is within the range of reported experimental values.[9,19]

The agreement between observed and calculated induction periods supports the choice of this model. It appears reasonable to attribute the limited temperature dependence of the explosion limits to the slow buildup of bromine atoms. The model does not account for, however, the variations in activation energies for the three mixtures that were studied extensively. Although they appear to be real, the scatter of data indicates that a minor systematic experimental error could be the cause of the variation. Pending further studies of this system and a more definite knowledge of the rate of Br atom recombination in this temperature range, it appears unwise to attach any significance to these activation energy variations.

It is our conclusion that the use of low temperature kinetic data is valid for the prediction of the behavior of this high temperature phenomenon. The fact that such a prediction can be made, requiring no modification of low temperature rate constants or mechanism, suggests that a similar situation may obtain in other systems. It must be borne in mind, however, that the uncertainties of measurement and the simplifications made in the explosion calculations are large and could cause major revisions in the quantitative results presented here. It is doubtful, on the other hand, that these could vitiate the applicability of the model.

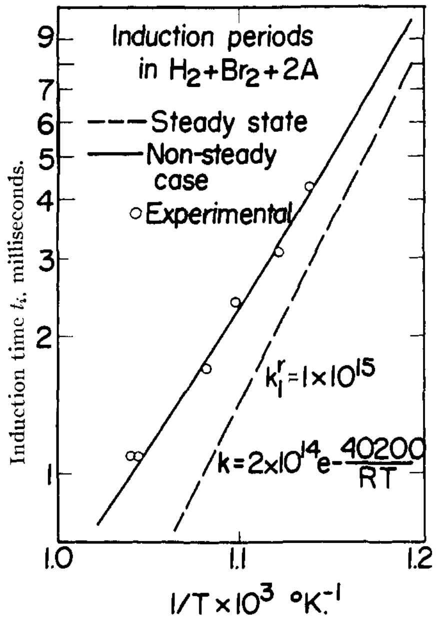

Fig. 4.—Induction periods in $H_2 + Br_2 + 2A$.

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Appendix

Rate and Explosion Equations—1. Adiabatic "Steady-State" Explosion.—In an insulated system, the heat release upon formation of HBr heats the gas mixture

$$[m]C_p\frac{dT}{dt} = \Delta H\frac{d[HBr]}{dt} \qquad (5)$$

where $[m]$ = total gas concentration, moles/cc., C_p = molar heat capacity, ΔH = enthalpy, cal./mole of HBr formed.

Assuming the steady-state rate expression (Table II) and that conversion is so slight that $[H_2]$ and $[Br_2]$ are constant and $[HBr] << [Br_2]$

$$\{[m]Cp(\Delta H[H_2][Br_2]^{1/2})\}dT/dt = k = A'e^{-E^*/RT} \qquad (6)$$

For convenience, we have set $k = 2 \times 10^{14}$ exp$(-40{,}200/RT)$ which has nearly the same value as Campbell's expression in the pertinent temperature range. Noting that the concentration terms are each inversely proportional to temperature, and substituting $z = E^*/RT$, and denoting the constant term by b

$$t_i = b(E^*/R)^{3/2}\int_{z_1}^{z_2}(e^z/z^{5/2})\,dz$$

$$= b(E^*/R)^{3/2}\,[(e^z/z^{5/2})\{1 + 5/2z + 35/4z^2 + 315/8z^3 + \cdots\}]_{z_1}^{z_2} \qquad (7)$$

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[19] K. Hilferding and W. Steiner, *Z. physik. Chem.*, **B30**, 399 (1935); E. Rabinowitch, *ibid.*, **B33**, 275 (1936).

in which this semi-convergent series is satisfactory for the values of z as encountered here. In practice $z_1 = E^*/RT_4$, $z_2 = E^*/R(T_4 + 100)$.

2. Isothermal Build-up of Bromine Atoms.—Using the mechanism in Table I, assuming that $[H_2]$ and $[Br_2]$ are constant, $[HBr] << [Br_2]$, and $[H] = (k_2[H_2]/k_3[Br_2])\,[Br]$, the rate expression for Br formation becomes

$$\frac{d([H] + [Br])}{dt} = \left(\frac{k_2[H_2]}{k_3[Br_2]} + 1\right)\frac{d[Br]}{dt} = k_1{}^{f}[m][Br_2] - k_1{}^{r}[m][Br]^2 \cong \frac{d[Br]}{dt}$$

since if $[H_2] \cong [Br_2]$, $k_2[H_2] << k_3[Br_2]$. Then

$$[Br] = \left(\frac{k_1{}^{f}[Br_2]}{k_1{}^{r}}\right)^{1/2} \tanh At \qquad (8)$$

where $A = (k_1{}^{f}k_1{}^{r}[Br_2]^{1/2})\,[m]$ and the integration is from $t = 0$ to $t = t$. The rate expression for HBr formation then becomes

$$\frac{d[HBr]}{dt} = 2k_2\,[H_2][Br] = 2S \tanh At \qquad (9)$$

If the end of the induction period is set at $t = 2/A$, at which time [Br] has reached 96% of its steady-state value, $[HBr] = 2S/A \ln \cosh 2$. During the same period, the steady-state reaction produces $[HBr] = 4S/A$. Numerically, the results of this integration are in good agreement with the approximate method developed by Matsen.[20]

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Hydrolysis of Ethylene Oxide Derivatives in Deuterium Oxide–Water Mixtures[1]

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The hydrolysis of several simple epoxides by the acid-catalyzed, the base-catalyzed and the uncatalyzed hydrolysis paths has been studied in deuterium oxide–water mixtures as solvent. For the acid-catalyzed reaction k_{D_2O}/k_{H_2O} varies from 1.9 to 2.2 and data for intermediate mole fractions of deuterium fit the Nelson and Butler theory quite well. It is concluded that this reaction involves a preliminary equilibrium proton transfer. For the base-catalyzed reaction the effect of deuterium oxide as solvent is small, k_{D_2O}/k_{H_2O} varying from *ca.* 1.0 to 1.1. This is consistent with the accepted SN2 mechanism. For the uncatalyzed hydrolysis the values of k_{D_2O}/k_{H_2O} vary from 0.8 to 0.9. This result serves to eliminate a mechanism which involves reaction of the conjugate acid form of the epoxide with hydroxide ion. However, it does not appear to permit a distinction between possible *S*N1 and *S*N2 reactions of epoxide with solvent.

Introduction

Deuterium isotope effects on the kinetics of reactions frequently have been used to elucidate reaction mechanisms. In some cases deuterium is substituted for hydrogen in a reactant organic molecule; in others a protonated solvent is replaced by a deuterated solvent, for example water is replaced by deuterium oxide. Wiberg[2] has recently reviewed both types of application and in particular has tabulated data on the effect of deuterium oxide as solvent on rates of various hydrolytic reactions catalyzed by either acids or bases. Some of the latter data are reproduced in Table I for reactions which are relevant to the present study. The mechanism classifications in the third column of Table I are based on the work of several investigators and are reasonably well established.

One deficiency in the investigations to date is that the magnitudes of the deuterium oxide solvent effects have not been adequately studied either for variations of hydrolysis mechanism within a given class of compounds or for effects of variation of structure for a given mechanism. In these respects an interesting field of study is the hydrolysis of epoxides. These compounds undergo hydrolysis by three distinct paths[3] and the mechanisms are well understood for at least two of the three. We have determined the effects of deuterium oxide on the rates of these reactions by dilatometric meas-

TABLE I

EXAMPLES OF SOLVENT DEUTERIUM OXIDE ISOTOPE EFFECTS IN HYDROLYTIC REACTIONS

Reactant	Catalyst	Mechanism class	T, °C.	k_{D_2O}/k_{H_2O}[2]
Ethyl orthoformate	H^+	A-1[10]	25	2.35
Acetal	H^+	A-1[10]	15	2.68
Sucrose	H^+	A-1[4]	25	2.05
Ethyl formate	H^+	A-2[5]	15	1.37
Ethyl acetate	H^+	A-2[5]	. .	1.49[6]
Methyl acetate	H^+	A-2[5]	15	*ca.* 1.7
Acetamide	H^+ (0.1 *M*)	A-2[7,8]	25	1.45
Acetamide	OH^-	SN2[7,8]	25	0.91
Ethyl acetate	OH^-	$B_{Ac}2$[6]	. .	1.33
Methyl iodide	None	SN2[8]	52.5	1.0[9]
Methyl chloride	None	SN2[8]	52.5	1.0[9]
t-Butyl chloride	None	SN1[8]	25.2	0.7[9]

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[1] Work supported by a grant from the Atomic Energy Commission.

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