Vibrational contributions to entropy were neglected both for the reactant diatomic molecule and for the transition state. This decision was taken because the known preexponential term for the reaction of $Br + H_2$ could be fitted well by the other assumptions without any consideration of vibration. This transition state is particularly "stiff," and vibrational entropy is probably more significant in some of the other reactions. Inclusion of vibration would increase the importance of the atomic chain mechanism for some reactions of halogen molecules but would not significantly affect the mechanistic conclusions.

Four-Atom Transition States. Every four-atom transition state was assumed to be planar. By employing the following symmetry numbers, the correction of Bishop and Laidler[16] was formally taken care of. For A_4 transition states, the symmetry number was four and the rate was written as $k[A_2]^2$. For A_2B_2 transition states, the symmetry number of two was used regardless of whether atoms of the same element were on opposite or adjacent corners. Symmetry numbers for all other transition states were assumed to be unity.

Transition states with formula A_4 were assumed to be square. Those with formula A_3B had AB and AA diagonals with lengths in the same ratio as the bond lengths of those molecules. Those with formulas A_2B_2 and like atoms on opposite corners were rhombohedral with diagonals in the ratio of AA and BB bond lengths; those with like atoms on adjacent corners had AA and BB sides parallel. For other transition states, the longest side and the one opposite were assumed to be parallel. For each transition state, moments of inertia were computed with the lengths of the sides equal to appropriate molecular internuclear distances, and the value of $(I_aI_bI_c)^{1/2}$ so obtained was multiplied by a factor of three to take care of bond expansion during formation of the transition state.

Electronic entropies were assumed to be zero for all transition states except those that could be formed from oxygen or nitric oxide; these had the minimum values to be expected from multiplicities if no electron spins were reversed.

Four of the five vibration frequencies of the transition state were each set equal to 0.40 times the frequency of the diatomic molecule appropriate to one of the four sides, and the fifth frequency was set equal to twice the minimum of the other four frequencies. Entropy contributions were then calculated. This treatment gave a fair fit to the observed entropy of activation for the reaction of hydrogen and iodine and a rather poor fit for nitric oxide decomposition. The method is certainly very crude but can be applied easily to a large number of reactions.

Reactions of Diatomic Molecules. III. Kinetics of Formation of Iodine Bromide

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Abstract: Iodine and bromine in carbon tetrachloride at 26.3° react by a bimolecular mechanism with rate constant of 510 l./mole sec. This is the first quantitative kinetic study of a halogen–halogen reaction, and the result is in good agreement with recent calculations indicating that such reactions should proceed by bimolecular mechanisms.

It has been predicted[1] that all reactions of halogens with halogens will take place by bimolecular rather than atomic chain mechanisms. No such reaction has received a detailed kinetic study.

The reaction of iodine with bromine to form IBr was selected for preliminary study because it was predicted[1] to be among the most rapid of the halogen–halogen reactions. This prediction was supported by qualitative observations of carbon tetrachloride solutions by Forbess and Schoonover at the University of Oregon and by a single stopped-flow measurement by Sturtevant at Yale University. In this paper, we report more extensive stopped-flow measurements in the same solvent.

Experimental Section

Reagent grade iodine was further purified by slow sublimation. Reagent grade bromine was shaken with concentrated sulfuric acid and distilled. The solvent was reagent grade carbon tetrachloride that had been distilled three times from phosphorus pentoxide.

Solutions of the halogens were analyzed spectrophotometrically with the use of the extinction coefficients reported by Tilich.[2]

The stopped-flow apparatus was based on the designs of Gibson[3] and Sutin.[4] Solutions came in contact only with glass and Teflon. The transmittance of the reaction mixture was monitored during reaction by a photomultiplier tube receiving light of 5400 A provided by the light source and monochromater of a Beckman DU spectrophotometer. The output from the photomultiplier was then put on a Tektronix 561A oscilloscope and the trace was photographed. The temperature of the room was kept at 26.3° during the runs.

Results

Let k be the rate constant in the forward direction for the bimolecular reaction

$$I_2 + Br_2 \longrightarrow 2IBr \tag{1}$$

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[1] R. M. Noyes, *J. Am. Chem. Soc.*, **88**, 4318 (1966).

[2] L. S. Tilich, *J. Gen. Chem. USSR*, **22**, 795 (1952).

[3] Q. H. Gibson, *Discussions Faraday Soc.*, **17**, 137 (1954).

[4] N. Sutin and B. M. Gordon, *J. Am. Chem. Soc.*, **83**, 70 (1961).

and let K be the equilibrium constant for the same reaction written as reversible. Let a and b be the initial concentrations of I_2 and Br_2, respectively, and let x be the concentration of IBr at time t. Then

$$k = \frac{1}{m}\frac{\mathrm{d}}{\mathrm{d}t}\ln\left(\frac{\dfrac{a+b+m}{1-4/K}-x}{\dfrac{a+b-m}{1-4/K}-x}\right) \qquad (2)$$

where

$$m = [(a+b)^2 - 4ab(1-4/K)]^{1/2} \qquad (3)$$

Values of k obtained for several runs are reported in Table I. The calculations assumed $K = 244$ based on the data of Popov and Mannion,[5] but the computed rate constant is rather insensitive to this value, particularly when the two reactants differ in concentration.

Table I. Kinetics of Iodine Bromide Formation

$[I_2]_0$, M	$[Br_2]_0$, M	k, l./mole sec
0.00298	0.00233	605
0.00298	0.00467	579
0.00298	0.00801	946
0.00296	0.0151	606
0.00281	0.0300	621
0.00263	0.0583	605
0.00271	0.00714	574
0.00790	0.00295	412
0.0162	0.00255	384
0.0297	0.00269	456
0.00771	0.00231	478
0.00376	0.00192	538
0.00128	0.00288	412
0.000540	0.00288	372

The data obey the anticipated kinetics. The highest k value satisfies statistical criteria for rejection, and the average of the other 13 runs is 510 l./mole sec. The standard deviation of a single determination is 95 l./mole sec.

Discussion

Presumably the only possible mechanisms for this reaction are the bimolecular elementary process and the atomic chain. It is possible to calculate the concentration of iodine atoms due to thermal and photochemical dissociation by the monitoring light and to estimate the rate of the chain process if the activation energy is the 3.6 kcal/mole difference in bond energies of Br_2 and IBr. The concentration of free atoms is insufficient by several orders of magnitude to account for the observed rate. Hence even an approximate estimate of half-life is sufficient to establish the mechanism unequivocally in this system.

Calculations based on the properties of reactant and product molecules[1] predicted an Arrhenius activation energy of 7.5 kcal/mole and a rate constant at this temperature of 161 l./mole sec. The agreement within a factor of about three is very gratifying. Application of the same calculation to hydrogen iodide synthesis[1] gave a preexponential term one-fifth of that observed; therefore the estimation of activation energy for iodine bromide synthesis may turn out to be very good indeed.

Benson and Haugen[6] by an entirely independent method predict an activation energy of 40.2 kcal/mole for the same reaction. This value can be accommodated to the observed rate only if the preexponential factor has the exceptionally large value of 10^{32} l./mole sec. Unless the solvent effect is much greater than there is any reason to expect, the Benson and Haugen method gives an unsatisfactory description of this system.[7]

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(5) A. I. Popov and J. J. Mannion, *J. Am. Chem. Soc.*, 74, 222 (1952).

(6) S. W. Benson and G. R. Haugen, *ibid.*, 87, 4036 (1965).

(7) Note Added in Proof. S. W. Benson (private communication) finds that in gas phase the same reaction is very rapid and apparently surface catalyzed. Subsequent experiments at the University of Oregon have shown that it is much slower in sulfuric acid than it is in carbon tetrachloride but that it is still too rapid to be proceeding by an atomic chain mechanism. The visible spectra of the molecules are virtually identical in all three phases. Although the homogeneous rate in truly "inert" solvent is not yet identified with certainty, the mechanistic conclusions of the paper appear to be unequivocal.