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Kinetics of Iodine Bromide Formation in Concentrated Sulfuric Acid. A Concerted Termolecular Process

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Abstract: The reversible reaction $I_2 + Br_2 \rightleftarrows 2IBr$ has been studied in 96% aqueous sulfuric acid. The rate in the forward direction is described empirically by $v = k_{ex}[I_2]_0[I_2][Br_2]$, where $[I_2]_0$ is *initial* iodine concentration and the other concentrations are *instantaneous*. The temperature dependence is given by $\log k_{ex} = 5.5 - (1.5/\theta)$, where k_{ex} is in liter^2 mole^{-2} second^{-1}, and θ is $2.30RT$ in kcal/mol. The observations can be explained if three halogen molecules undergo a concerted process in which bonds are simultaneously broken and formed. Since only two of the three product molecules can differ chemically from reactant molecules, the process is essentially halogen molecule catalysis of a net bimolecular reaction. The data require that Br_2 be much less efficient than I_2 as a catalyst and that IBr be almost exactly half as efficient as I_2. The rapid second-order reaction of iodine with bromine in carbon tetrachloride is not the bimolecular process that it was once thought to be but involves some sort of catalysis, probably by adventitious moisture. Suppression of this catalysis in the strongly dehydrating solvent sulfuric acid permits observation of halogen molecule catalysis. The need for three rather than two molecules of halogen in the transition state is consistent with the orbital symmetry arguments of Woodward and Hoffmann.

In principle, the simplest one-step reaction of stable molecules should be of the form

$$A_2 + B_2 \longrightarrow 2AB \tag{1}$$

where A and B are single monovalent atoms held to their partners by σ bonds. In practice, this net chemical change usually seems to take place by a more complex mechanism.

Let v_b be the rate of the gas-phase elementary bimolecular process described by eq 1, and let v_{obsd} be the total rate of all mechanisms by which the net reaction is observed to take place in a real system. No surface that leaves the major fraction of gas molecules unadsorbed and no impurity present in trace amounts can conceivably *reduce* the rate of any elementary bimolecular process involving major components of the system; the only possible kinetic influences are catalytic *increases* in rate. Therefore, for all observations on gaseous systems, we can state unequivocally that

$$v_{obsd} \geq v_b \tag{2}$$

Although eq 2 is not as incontrovertibly valid for reactions in solution, any v_{obsd} in solution must be at least as great as the hypothetical gas-phase v_b unless the reactants A_2 and B_2 are solvated more strongly than is the transition state for the elementary bimolecular process. The above arguments imply that the search for an example of such an elementary bimolecular process is related to the search for conditions giving the slowest possible rate in the gas phase or in a solvent that does not solvate the reactants strongly.

The reaction chosen for the present study was

$$I_2 + Br_2 \rightleftarrows 2IBr \tag{3}$$

which previous calculations[1] suggested would be one of the most facile examples of the desired reaction type. Previous observations[2] had also indicated a rapid reaction of the expected kinetics in dried carbon tetrachloride. However, subsequent observations demonstrated a much slower rate in concentrated sulfuric acid solvent. Therefore, unless the ground states are preferentially solvated in this medium, the argument of eq 2

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(1) R. M. Noyes, *J. Amer. Chem. Soc.*, **88**, 4311, 4318 (1966).

(2) P. R. Walton and R. M. Noyes, *ibid.*, **88**, 4324 (1966).

indicates the reaction in carbon tetrachloride is strongly catalyzed and is not an example of an elementary bimolecular process. Some observations in sulfuric acid solvent are reported in the present paper.

Experimental Section

Reagent grade bromine, iodine, and 96% sulfuric acid were used directly without further purification. Concentrations of solutions were determined either titrimetrically or spectrophotometrically.

The titrimetric procedure was the ultimate standard. It involved placing a known volume of solution in a side arm of a stoppered flask containing a large excess of ice in the main compartment. The acid was then tipped onto the ice, and the resulting cooled solution was treated with a solution of sodium acetate and potassium iodide and titrated with standardized sodium thiosulfate.

Because the titration procedure was cumbersome, most solutions were analyzed spectrophotometrically with the use of extinction coefficients determined from titrimetrically analyzed solutions. Beer's law was obeyed well in the visible region. In the ultraviolet, an absorption approximately proportional to the square root of halogen concentration was ascribed to small amounts of halide ions. As shown by the argument in the introduction, these ions could only have accelerated and not retarded the rate of the reaction being studied. Therefore, any ionic contributions to the rate in sulfuric acid would make the much faster rate in carbon tetrachloride still harder to explain.

All kinetic runs reported here were observed at 520 nm. Extinction coefficients at this wavelength (defined by the standard log $I_0/I = \epsilon cl$) are presented in Table I for iodine and bromine at the temperatures of interest. Measurements on equilibrium mixtures from known initial compositions were used to solve simultaneous equations giving ϵ_{IBr} and K, the equilibrium constant for eq 3. These results are also presented in Table I. Extreme accuracy was not attempted in these equilibrium measurements because reaction is so nearly complete that an error of even a factor of 2 in K would scarcely affect the rate constant calculated from a run followed for up to two half-lives.

Table I. Extinction Coefficients at 520 nm [l./(mol cm)] and Equilibrium Constants for IBr Formation

Phase	96% H_2SO_4			CCl_4	Gas
Temp, °C	15.0	25.0	40.0	25.0	25.0
ϵ_{I_2}	703	702	692	910[a]	830[b]
ϵ_{Br_2}	34.7	36.3	36.4	64[a]	46.2[c]
ϵ_{IBr}	157	159	166	293[a]	270[c]
K	298	270	262	372,[d] 1017[a]	482[e]

[a] A. I. Popov, K. C. Brinker, L. Campanaro, and R. W. Rinehart, *J. Amer. Chem. Soc.*, **73**, 514 (1951). [b] Based on estimate of figure drawn by E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 540 (1936). [c] D. J. Seery and D. Britton, *J. Phys. Chem.*, **68**, 2263 (1964). [d] D. M. Yost, T. F. Anderson, and F. Skoog, *J. Amer. Chem. Soc.*, **55**, 552 (1933). [e] W. H. Evans, T. R. Munson, and D. D. Wagman, *J. Res. Nat. Bur. Stand.*, **55**, 147 (1955).

Table I also contains values of extinction coefficients and equilibrium constants reported for the gas phase and carbon tetrachloride solution. These comparative values are considered further in the Discussion section.

For a kinetic run, halogen solutions of known concentration were mixed and placed in optical cells with 5-cm light paths. The cells were thermostated, and absorbance at 520 nm was measured with a Beckman spectrophotometer at frequent intervals for periods up to about 1 hr. Titration of the solution after a run usually accounted within 2% for the halogen known to have been present initially.

Results

Initial and infinite time absorbances could be calculated with the use of data from Table I. Absorbances at intermediate times could be fitted to the standard expression for kinetics of a reversible second-order reaction.[3] The appropriate function exhibited excellent linearity for at least about two half-lives; deviations at longer times could not be separated from effects associated with the 2% uncertainty in total halogen referred to above. The rate of reaction, v, in any run could therefore be described by a second-order rate constant, k_2, according to the expression

$$v = (1/2)\frac{d[IBr]}{dt} = k_2\{[I_2][Br_2] - [IBr]^2/K\} \qquad (4)$$

However, values of k_2 at any temperature depended strongly upon the concentrations of reactants and varied from run to run. Data for all runs could be fitted fairly satisfactorily by an experimental rate constant k_{ex}, defined by the equation

$$v = k_{ex}[I_2]_0\{[I_2][Br_2] - [IBr]^2/K\} \qquad (5)$$

where $[I_2]_0$ is the *initial* concentration of iodine for the particular run.

The kinetic observations are summarized in Table II.

Table II. Kinetic Data for IBr Formation in Sulfuric Acid

Temp, °C	$10^4[I_2]_0$, M	$10^4[Br_2]_0$, M	k_2, l./(mol sec)	$10^{-4}k_{ex}$, (l./mol)^2 sec^{-1}
15.0	2.332	1.070	6.83	2.93
	2.128	2.156	5.85	2.75
	1.035	1.030	2.03	1.96
	0.980	0.990	2.09	2.13
	1.133	2.288	2.60	2.29
				Av 2.41
25.0	1.285	6.570	3.67	2.86
	2.618	2.619	6.67	2.55
	1.705	5.200	5.53	3.24
	1.830	5.460	4.09	2.23
	1.830	5.460	4.42	2.42
	2.375[a]	2.362[a]	6.33[a]	2.67[a]
	1.123[a]	6.680[a]	3.40[a]	3.03[a]
	2.300	2.294	7.35	3.20
	2.264	1.134	5.46	2.49
				Av 2.74
40.0	2.390	2.400	7.59	3.18
	2.344	0.940	6.27	2.67
				Av 2.92

[a] Run in 98% H_2SO_4.

The temperature dependence of the k_{ex} values can be fitted by the equation

$$\log k_{ex} = 5.5 - (1.5/\theta) \qquad (6)$$

where θ is $2.303RT$ in kcal/mol. The numerical value of the preexponential factor is intermediate between those for third-order reactions of nitric oxide and those for third-order processes in which one molecule catalyzes a combination of the other two.[4]

Discussion

Mechanism of the Reaction. It is unusual but by no means unprecedented to find that the empirical equation for reaction rate depends upon the initial rather than the instantaneous concentration of a species whose concentration is changing during reaction.

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[3] See, for example, A. A. Frost, and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 187.

[4] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 310.

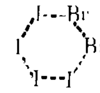
Table III. Free Energy Changes (at 25°) for Solvation and Reaction

Phase	96% H_2SO_4	H_2O	CCl_4	Gas
$\Delta G°_{solv}$ (I_2), kcal/mol	−1.91	−2.59[a]	−5.39[a]	0.000
$\Delta G°_{solv}$ (Br_2), kcal/mol	(−0.98)[b]	−1.66[a]	−3.66[a]	0.000
K	270		372[c]	482[d]
$\Delta G°$ (eq 3), kcal/mol	−3.32		−3.51[c]	−3.66[d]
$\Delta G°_{solv}$ (IBr), kcal/mol	(−1.28)[b]		−4.45	0.000
k, l./(mol sec)	1.3 (max bimolecular) 11.6 (I_2 satd)		510[e]	
$\Delta G^{\ddagger}$, kcal/mol	17.31 (min bimolecular) 16.00 (I_2 satd)		13.76[e]	

[a] A. Seidell, "Solubilities of Inorganic and Metal-Organic Compounds," Vol. 1, 4th ed, revised by W. F. Linke, D. Van Nostrand, Princeton, N. J., 1958. [b] Based on the assumption that the iodine and bromine solvation free energies differ by the same amount in water and in sulfuric acid. [c] D. M. Yost, T. F. Anderson, and F. Skoog, *J. Amer. Chem. Soc.*, **55**, 552 (1933). [d] W. H. Evans, T. R. Munson, and D. D. Wagman, *J. Res. Nat. Bur. Stand.*, **55**, 147 (1955). [e] P. R. Walton and R. M. Noyes, *J. Amer. Chem. Soc.*, **88**, 4324 (1966).

Whenever such a situation occurs, the product species must have approximately the same kinetic influence as the reactant from which it is derived. When a nearly thermoneutral reaction takes place with an activation energy of only 1.5 kcal/mol, an additional mechanistic requirement is that breaking and formation of bonds occur by concerted processes.

The results indicate that for a solution containing only iodine and bromine molecules, the *initial* rate is second order in iodine and first order in bromine. Such kinetics are consistent with a transition state of the form



A

If three bonds are formed and three are broken in a concerted process, the net consequence is an iodine molecule catalysis of eq 3.

It is equally possible to write structures similar to A by which Br_2 and IBr molecules can catalyze reaction 3. Let k_{I_2}, k_{Br_2}, and k_{IBr} be the rate constants for these three independent termolecular elementary processes. Then the rate in terms of *instantaneous* concentrations should be given by

$$v = \{k_{I_2}[I_2] + k_{Br_2}[Br_2] + k_{IBr}[IBr]\}\{[I_2][Br_2] - [IBr]^2/K\} \quad (7)$$

In order to accomodate the apparent independence of the rate from bromine concentration, it is necessary that

$$k_{I_2} \gg k_{Br_2} \quad (8)$$

Since individual runs obey second-order kinetics without evidence of drift, two IBr molecules must have almost the same catalytic efficiency as did the I_2 molecule from which they were produced. Hence

$$k_{I_2} = 2k_{IBr} \quad (9)$$

appears to be a good but probably fortuitous approximation. If these restrictions are applied, substitution of $[I_2] + \frac{1}{2}[IBr] = [I_2]_0$ shows that eq 7 is consistent with the empirical eq 5.

Evidence against Heterogeneity. The above discussion has been based on the assumption that the observed reaction is indeed homogeneous. It is not easy to increase surface greatly in a reaction that is being followed spectrophotometrically, but two different cell sizes were used. The first seven runs at 25° in Table II were made in cells having about 10-mm diameters, and the other two runs at this temperature and the runs at higher and lower temperatures were made in cells having about 20-mm diameters. The data do not show any evidence for an effect of change in surface area.

The rapidity of the reaction is probably the best evidence against heterogeneity. The half-life was about 400 sec (less than 7 min) for the runs with largest excess of bromine. The sulfuric acid has a viscosity of about 20 cp and a coefficient of thermal expansion less than half that of most organic solvents. No conceivable combination of diffusion and convection in such a solvent could that rapidly bring half the solute molecules to the walls of a thermostated 2-cm cylinder.

Implications for Bimolecular Mechanism. This research was initiated in the expectation that the reaction would be *bimolecular*. The experimental data demonstrate that most of the product is formed by a concerted *termolecular* process. An indication of possible bimolecular contribution is obtained by fitting k_2 of eq 4 to an expression of the form

$$k_2 = k_a + k_b[I_2]_0 \quad (10)$$

A least-squares fit of the data at 25° gives $k_a = 0.58 \pm 0.68$ l./(mol sec), where the indicated uncertainty is 50% confidence based on scatter of individual points from the best line. The more limited data at 15° indicate a physically impossible *negative* value of k_a. The data clearly do not indicate any significant contribution from the bimolecular mechanism, although the scatter is so great that the only limit we can set is that at 25° the maximum plausible value for k_a is k_a(max) = 1.3 l./(mol sec). This number is very much less than the second-order rate constant of 510 l./(mol sec) reported[2] in carbon tetrachloride solvent.

According to the argument developed in the introduction, the fast reaction in carbon tetrachloride cannot be truly bimolecular unless the difference from sulfuric acid can be explained by solvation effects. Free energy data based on reported solubilities are presented in Table III, where $\Delta G°_{solv}(X_2)$ is the free energy of solvation of X_2 compared to gaseous material *at the same concentration*. The value calculated for I_2 in sulfuric acid is based on the vapor pressure and our measured solubility of 0.000416 mol/l., in good agreement with a reported[5] solubility of 0.000423 mol/l. We did not

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(5) A. Seidell, "Solubilities of Inorganic and Metal-Organic Compounds," Vol. I, 4th ed, revised by W. F. Linke, D. Van Nostrand, Princeton, N. J., 1958, p 1275.

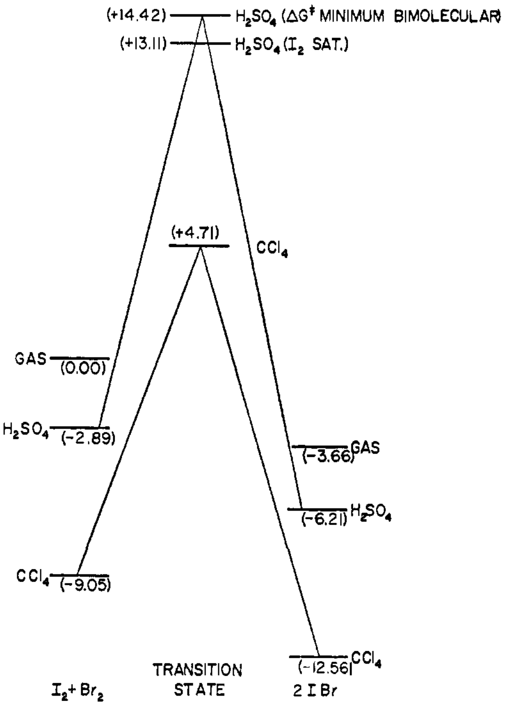

Figure 1. Free energies (at 25° with standard states in *M*) for reactions of iodine and bromine in different media. Numbers associated with different states are free energies of formation (kcal/mol) from gaseous elements and pure solvent.

measure the solubility of bromine in our solvent but have assumed that solvation free energies of bromine and of iodine differ by the same amount in sulfuric acid as they do in water; the assumption can hardly be in error by more than 0.5 kcal/mol. As would be expected, the polarizable heavy halogens are solvated more strongly by the "soft" carbon tetrachloride than by the "hard" hydroxylic solvents.

The equilibrium constants, already reported in Table I, permit calculation of $\Delta G°$ for the overall reaction and hence of $\Delta G°_{\text{solv}}(\text{IBr})$. Values of k in Table III are observed or calculated second-order rate constants. The one designated as "max bimolecular" is the $k_a(\text{max})$ discussed in connection with eq 10. The one designated "I_2 satd" is the value of k_2 (see eq 4) calculated for a solution saturated with iodine and is hence the largest second-order rate constant that could be observed at this temperature in sulfuric acid solvent. The $\Delta G^{\ddagger}$ values are free energies of activation calculated for the second-order rate constants in the same table.

Free energies based on Table III are shown schematically in Figure 1. The free energy of the reactant $I_2 + Br_2$ in sulfuric acid is 6.16 kcal/mol more than in carbon tetrachloride, while the *minimum* free energy of a bimolecular transition state in sulfuric acid is 9.71 kcal/mol more than in carbon tetrachloride; the difference is more than the *total* free energy of solvation of $I_2 + Br_2$ in sulfuric acid. Therefore, if the fast second-order reaction in carbon tetrachloride is indeed bimolecular, the transition state must be solvated *more* strongly than the ground state. Since formation of a transition state requires displacement of some of the solvent molecules originally surrounding the reactant species, the transition state in carbon tetrachloride should, if anything, be solvated *less* strongly than the ground state. *We therefore conclude that the rapid reaction previously observed*[2] *in carbon tetrachloride involves some sort of catalysis and is not the bimolecular process we supposed at that time.*

Concluding Remarks

The interesting conclusion of this work is that a concerted process involving simultaneous breaking and forming of bonds is not easily accessible to two halogen molecules but can occur with very low activation energy in the superficially more complicated system of three halogen molecules. Such a result follows directly from the orbital symmetry arguments of Woodward and Hoffman,[6] and these observations must be added to the impressive accumulation of data supporting their insight.

We cannot yet explain the remarkable second-order rate constant of 510 l./(mol sec) when the reaction takes place in carbon tetrachloride.[2] That study was conducted under turbulent conditions in a stopped-flow apparatus where heterogeneous effects are hard to eliminate, but qualitative observations indicate that the homogeneous reaction is almost instantaneous when macroscopic volumes of solution are poured together. Hildebrand[7] reported a negative temperature coefficient for the rate of ICl formation in carbon tetrachloride and proposed catalysis by adventitious moisture. In the present study, we selected 96% sulfuric acid as a solvent in order to reduce the activity of water, and this selection permitted us to observe catalysis by the third halogen molecule. We do not yet have any suggestion as to why water molecules appear to be such efficient catalysts for these halogen–halogen reactions.

It should also be admitted at this time that effects of surface and of moisture are strongly implicated in the gas-phase reaction of chlorine with hydrogen bromide and that this reaction also is not as simple as was first thought.[8] Details will be reported when the system is better characterized, but we must concede failure to date in our search for homogeneous concerted bimolecular reactions of σ-bonded diatomic molecules.

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[6] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[7] J. H. Hildebrand, *J. Amer. Chem. Soc.*, **68**, 915 (1946).

[8] P. Goldfinger, R. M. Noyes, and W. Y. Wen, *ibid.*, **91**, 4003 (1969).