

Kinetics and Mechanism of Sonochemical Decomposition of Aqueous Bromoform Solution

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With 5 Figures

Abstract

Ultrasonic waves obtained from MULLARD's high frequency ultrasonic generator type E-7562 with a barium titanate transducer having a frequency of 1 Mc./sec. were employed to study the sonochemical decomposition of aqueous bromoform solution. At constant R. F. output (about 1.7 Kv) to the crystal, the reaction was found to obey the Zero-order kinetics with average velocity constants in standard unit as follows:

$$K_s (\text{Br}_2, \text{Br}^-) = 8.211 \cdot 10^{-5} \text{ gm. eq. lit.}^{-1} \text{ min.}^{-1}$$

$$K_s (\text{Br}_2) = 4.182 \cdot 10^{-5} \text{ gm. eq. lit.}^{-1} \text{ min.}^{-1}$$

Effects of bulk and ultrasonic intensity have also been demonstrated. The rate of reaction at different dilutions of aqueous bromoform solution and also at different intensities has been investigated conductometrically. A probable mechanism of the reaction was also presented.

In the study of effects produced by high intensity ultrasonic waves, it is well known that the phenomenon of cavitation, which refers to the formation and violent collapse of small bubbles or cavities in the liquid as a result of pressure changes, is able to bring about a variety of chemical reactions, including oxidation, reduction, polymerization, decomposition, hydrolysis, depolymerization and rearrangements. For the last 40 years or so much attention has been directed towards the chemical changes produced in liquids by these waves, but a fully satisfactory explanation of the effect is not yet available. The study of the sonochemical decomposition of aqueous solutions of some organic compounds has been a subject of much interest in this field and this problem has already been investigated by a number of workers. A good deal of data is available on the decomposition of aqueous

organic chloro compounds¹⁻⁶) by ultrasonic waves. Comparatively a very little work has been done on bromides. In order to get further insight into the nature of sonochemical reactions, the present authors have put in their best efforts to the study of kinetics and mechanism of decomposition of bromoform-water mixture by ultrasonic energy.

Experimental

A saturated solution (density 0.9965 gm./ml.), of distilled bromoform, E. Merck quality (density 2.8570 gm./ml., solubility in pure water 0.272 gm./100 ml., b.pt. 149.5°C and molecular weight 252.77) was prepared in re-distilled water (density 0.9938 gm/ml) Ultrasonic waves have been generated from MULLARD's high frequency ultrasonic generator type E-7562 with barium titanate transducer having frequency of 1 Mc/sec. It generates ultrasonic waves of radio frequency output voltage up to 10 kilo volts. The major portions of the experiments of the present paper were done at a fixed electrical output to the transducer, except when the effect of ultrasonic intensity was to be studied. The reaction vessel, which was a 250 ml. jena bottle with ground glass stopper, was suspended inside a constant temperature water tank, from a micrometer screw end and is clamped between two brass plates. The position of the bottle was so adjusted as to get maximum fountain.

20 ml. of the saturated bromoform solution were subjected to ultrasonic radiations for different times. 5 ml. of the exposed solutions were taken and estimated for free bromine and bromide ion. The results are recorded in table 1. The values of zero order velocity constants and amount of total bromine liberated were calculated from the titre values and are shown in table 2. The values are also calculated graphically (Fig. 1).

To observe the effect of volume on the sonochemical decomposition of bromoform, different volumes of its saturated solution were exposed to ultrasonic waves for 10 min. The results are shown in fig. 2. In fig. 3 the kinetics of the reaction at different dilutions of aqueous bromoform solution has been investigated conductometrically. Nextly the effect of ultrasonic intensity on bromine production was investigated. Saturated solution of bromoform was exposed to ultrasonic waves (for 5 mts) by increasing the R. F. output and the results obtained are shown in fig. 4. The kinetics of the reaction at three different R. F. output voltage has been studied conductometrically and the results are plotted in fig. 5.

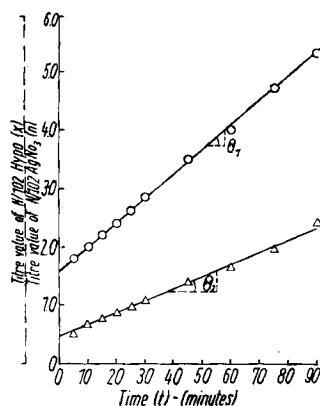


Fig. 1. Sonochemical decomposition of satd. Bromoform solutions- Zero order reaction.

$$k(\text{Br}^- + \text{Br}_2) = \tan \theta_1 = 0.0416$$

$$k(\text{Br}_2) = \tan \theta_2 = 0.0208$$

○ AgNO₃; △ Hypo

1) A. WEISSLER, H. W. COOPER and S. SNYDER, J. Amer. Chem. Soc. **72**, 1769 (1950).

2) A. KLING and R. LING, Compt. Rend. **223**, 1131 (1946).

3) S. PRAKASH and S. C. SRIVASTAVA, J. Indian Chem. Soc. **35**, 797 (1958).

4) S. PRAKASH and S. C. SRIVASTAVA, Z. physik. Chem. **208**, 127 (1957).

5) N. BERKOWITZ and S. C. SRIVASTAVA, Canad. J. Chemistry **41**, 1787 (1963).

6) S. C. SRIVASTAVA, Nature **182**, 47 (1958).

Table 1

Temperature = $22.3 \pm 0.2^\circ\text{C}$

R. F. output = 1.7 Kv (approx)

Amount of CHBr_3 present in 20 ml. of the solution = 0.0544 gm.

Time of exposure in minutes	Titre value of $N/102 \text{ AgNO}_3$ solution	Titre value of $N/102$ hypo-solution	Titre value for bromide ion [as HBr]
5	1.78	0.50	1.28
10	2.00	0.66	1.34
15	2.22	0.78	1.44
20	2.42	0.88	1.54
25	2.64	0.98	1.64
30	2.86	1.08	1.78
45	3.52	1.36	2.16
60	4.14	1.66	2.48
75	4.74	1.96	2.78
90	5.36	2.24	3.12

Table 2

Extrapolated from table 1

Time in minutes	Zero order velocity constant $K_0 = dx/dt$		Amount of bromine liberated per gm. mole of CHBr_3	Amount of bromide (as HBr) liberated per gm. mole
	I $K_0 (\text{Br}_2, \text{Br}^-)$	II $K_0 \text{ Br}_2$		
5			7.295	18.675
	0.044	0.032		
10			9.629	19.551
	0.044	0.024		
15			11.380	21.010
	0.036	0.020		
20			12.839	22.469
	0.044	0.020		
25			14.308	24.219
	0.044	0.020		
30			15.757	25.970
	0.044	0.018		
45			19.842	31.514
	0.041	0.020		
60			24.219	36.183
	0.040	0.020		
75			28.606	40.560
	0.041	0.018		
90			32.682	45.720

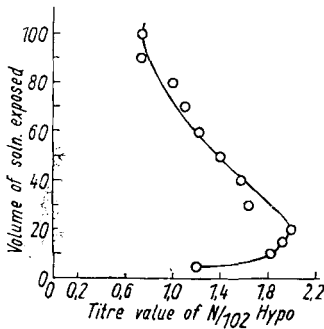


Fig. 2. Bulk Effect

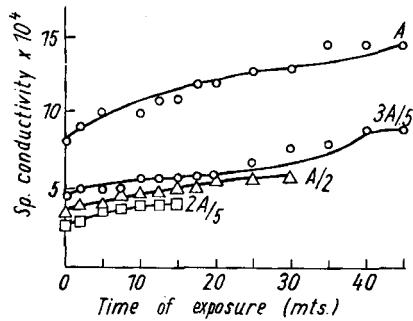


Fig. 3. Kinetics of the reaction conductometrically

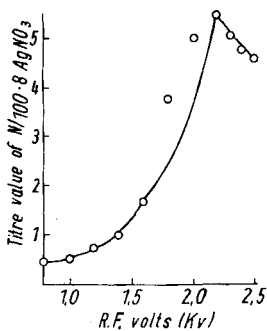


Fig. 4. Effect of intensity

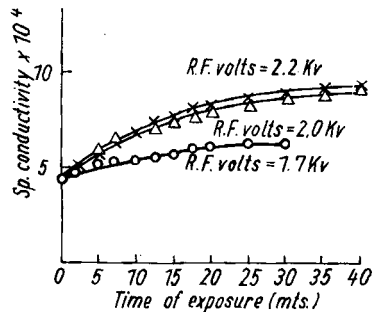


Fig. 5. Reaction kinetics at three different intensities

Discussion

From the results recorded in tables 1 and 2 it is clear that with the saturated solution of bromoform the amount of total bromine liberated per gm. mole in 90 minutes of ultrasonic exposure (R. F. output 1.7 Kv) is 78.402. The ratio of the bromine decomposed to the total bromine present in bromoform is found to be approximately 0.33. The production of bromine increases as the time of ultrasonic exposure is increased. Free bromine as well as bromine as bromide ion (as HBr) have been tested in exposed solution and also estimated from time to time. Out of the total bromine liberated in 90 min. of exposure, the amounts of Br_2 and Br^- were respectively 32.682 and 45,720gm. per mole. A perusal of the tables 1 and 2 as well as of the fig. 1 shows that the rate of sonochemical production of bromine follow the zero order kinetics with zero order velocity constants as:

$$k_0 (\text{Br}^-, \text{Br}_2) = 4.188 \cdot 10^{-2}$$

$$k_0 (\text{Br}_2) = 2.133 \cdot 10^{-2}$$

These values were also calculated graphically (fig. 1). The zero order velocity constant equation is

$$\frac{dx}{dt} = K_0$$

or in its integrated form $x = k_0 t + C$. The values of x (in terms of titrating agent volume required) are plotted against t , the time of exposure. The standard zero order velocity constants (k_s) in terms of titrating agent values are calculated from the relation.

$$k_s = \frac{s}{v} K_0$$

where s is the strength of titrating agent and v is the volume of aliquot.

$$k_s (\text{Br}_2, \text{Br}^-) = 8.211 \cdot 10^{-5} \text{ gm. eq. lit.}^{-1} \text{ min.}^{-1}$$

$$k_s (\text{Br}_2) = 4.182 \cdot 10^{-5} \text{ gm. eq. lit.}^{-1} \text{ min.}^{-1}$$

Effect of volume of reaction mixture exposed, on the sonochemical decomposition of aqueous bromoform solution, is shown in fig. 2. The amount of liberated bromine as well as bromide ion increases at first and then decreases on increasing the bulk of the solution. Finally it comes to a constant value as evident from the curve.

The next variable investigated was the effect of acoustic intensity. In fig. 4 the effect of increase of ultrasonic intensity in terms of radio frequency voltage (R. F. output) has been observed by keeping the time of exposure fixed. The total bromine has been estimated for five minutes exposure. Bromine liberation first increases by increasing the intensity and reaches a maximum value at 2.2 Kv. Further increase of intensity causes a decrease in the amount of bromine. The kinetics of the reaction at three different intensities were studied conductometrically and the results are shown in fig. 5. The reaction velocity increases by increasing the output power.

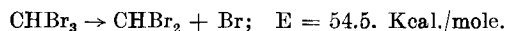
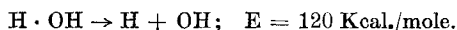
From theoretical consideration it may be concluded that the passage of ultrasonic waves through a liquid would generate cavitation bubbles only when the liquid contains any impurities either in the form of a solid or as gas. Nearly all the observed chemical effects of ultrasonic irradiation in liquid systems occur only at intensities sufficient to induce cavitation within the system. It is also observed experimentally that at very low intensities which are below the threshold for cavitation, no chemical change is noticed. At levels of ultrasonic intensity above the threshold for the onset of cavitation, reaction rates increase more or less in a linear manner. An optimum intensity has also been found which coincides with the maximum formation of cavitation holes, and above it further increases causes a decrease in the yield⁷⁾⁸⁾.

⁷⁾ O. LINDSTRÖM, J. Acoust. Soc. Am. **27**, 654 (1955).

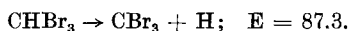
⁸⁾ A. WEISSLER, J. Acoust. Soc. Am. **25**, 651 (1953).

The vigorous cavitation causes so much removal of dissolved air that the residual amount is insufficient to maintain the reaction at its maximum speed.

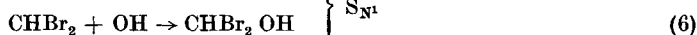
According to the physical picture of cavitational phenomena one would expect that the vapour of the solvent as well as that of the solute (in the case of liquid solute) will be present inside the cavitational bubbles. Consequently the collapse of these bubbles would impart similar physical conditions (temperature and pressure) on the molecules of both the liquid and vapours. It is likely that both the vapours undergo decomposition simultaneously. Energy considerations also suggest that if H_2O can undergo homolytic dissociation, CHBr_3 molecules, should likewise experience primary cleavage. So, it is clear that the homolytic dissociation of water as well as bromoform takes place simultaneously as the primary step, namely:



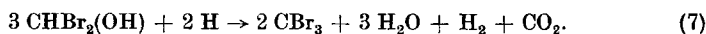
Due to high resonance energy of CHBr_3 , the following reaction may also occur in addition to above:



At this point it is important to consider the work of J. HIRE⁹) who has discussed the relative reactivity of CCl_4 , CHCl_3 etc. under various conditions and suggested three alternative mechanisms for the hydrolysis of chloroform. Applying this analogy to bromoform also ($\text{C}-\text{Cl} > \text{C}-\text{Br}$) the hydrolysis of bromoform by ultrasonic waves may also be formulated likewise. But this needs careful scrutiny before it can be applied for the hydrolysis of CHBr_3 . In order to explain the various steps after the primary reactions 1, 2 and 3 at least so far as the hydrolysis is concerned, a better approach may be made by considering the mechanisms of substitution at a saturated carbon atom as proposed by HUGHES, INGOLD and coworkers¹⁰). They have proposed S_{N} and S_{E} chains for these types of reactions. Considering these, the probable mechanism of bromoform decomposition as promoted by ultrasonic waves, may be proposed as follows:



followed by



⁹) J. HIRE, J. Amer. Chem. Soc. 72, 2438 (1950).

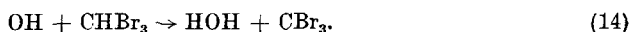
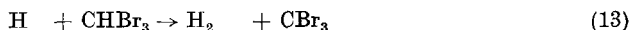
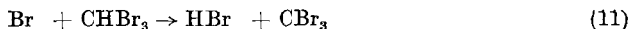
¹⁰) C. K. INGOLD and E. D. HUGHES, J. Chem. Soc. London 225 (1936); 225 (1935) and 1183 (1937).

¹⁰ J. prakt. Chem. 4. Reihe, Bd. 26.

The other radicals may react:

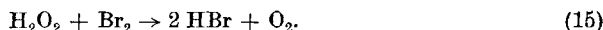


Br, H and OH radicals may also react as proposed by JENNINGS and TOWNSEND¹¹⁾ for CHCl_3 decomposition:

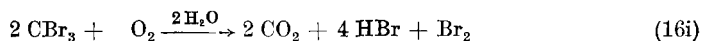


The radical CHBr_2 may also react with H otherwise to form CH_2Br_2 which further decomposes. The presence of CBr_3 and CHBr_2 has been shown by JENNING and TOWNSEND¹¹⁾ as CCl_3 and CHCl_2 in CHCl_3 system. Here it is assumed to be true for CHBr_3 . Br_2 and Br is estimated here.

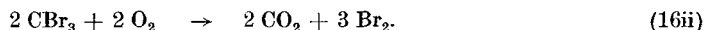
Any H_2O_2 formed in reaction was consumed as:



The presence of oxygen may give the following reaction:



or



The presence of hexachloromethylene and tetrachloromethylene has also been shown by JENNINGS and TOWNSEND in CHCl_3 decomposition. Likewise, hexabromomethylene and tetrabromomethylene can also be formed as:



¹¹⁾ B. H. JENNINGS and S. N. TOWNSEND, J. Phys. Chem. **65**, 1574 (1961).

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