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SONOCLEAVAGE OF HALOGENS FROM ALIPHATIC CHAINS AND AROMATIC RINGS

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Abstract—Liberation of halogen atoms from aqueous solutions of some aliphatic and aromatic halogen compounds by ultrasonic waves has been investigated. The kinetics of the sonochemical decomposition in all cases obeys the zero-order reaction. On exposure to ultrasound, aromatic halogen compounds yield the halogen in the form of acids whereas aliphatic compounds liberate both free halogen and hydrogen halides. A probable mechanism for these reactions is proposed. In the case of aromatic compounds, the proposed mechanism is based on the work of Zechmeister *et al.*, and others who have detected experimentally the presence of acetylene and some diacetylene in addition to halogens and other products. The results are discussed on the basis of cavitation phenomenon which is supposed to be responsible for all the observed sono-chemical effects. Sonocleavage of halogen atoms from these compounds is only achieved in the presence of water.

IN THE present communication some results of an investigation on halogen break down from some aliphatic chains and aromatic rings is reported. The liberation of halogen atoms from aromatic monohalogen derivatives by ultrasonic waves was first detected by Weissler.[1] In recent papers, Zechmeister *et al.*[2–3] have described methods for separation, identification and quantitative estimation of the aromatic ring cleavage products. They have shown that when the molecules of bromobenzene and other aromatic compounds are subjected to ultrasonic radiations, the presence of acetylene and some diacetylene is indicated. This process may be considered the reverse, at room temperature, of Berthelot's synthesis of benzene from acetylene. Currell *et al.*[4] have also studied the effect of certain variables on the ultrasonic cleavage of phenol and pyridine rings. The mechanism of sonochemical decomposition of some aliphatic halogen compounds in aqueous solution have been proposed recently by Jennings *et al.*[5] and by Srivastava *et al.*[6–8]

EXPERIMENTAL

A saturated aqueous solution of each of the following (B.D.H. quality) was used: *ethyl iodide* (mol. wt. = 155·98, $d = 1{\cdot}9330$ gm/ml at 20° and solubility in water = 0·158 gm/100 ml), *iodobenzene* (mol. wt. = 204·02, $d = 1{\cdot}832$ gm/ml and solubility = 0·02 gm/100 ml) and *o-dichlorobenzene* (mol. wt. = 147·01, $d = 1{\cdot}303$ gm/ml and solubility = 0·0146 gm/100 ml). Ultrasonic waves were obtained from a Mullard's high frequency ultrasonic generator type E-7562 with a barium

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[1] A. Weissler, *Chem. Eng. Prog. Symp.* No. 1 and 2, 22 (1951).

[2] L. Zechmeister and L. Wallcave, *J. Amer. Chem. Soc.* **77**, 2853 (1955).

[3] L. Zechmeister and D. L. Currell, *J. Amer. Chem. Soc.* **80**, 205 (1958).

[4] D. L. Currell, G. Wilheim and S. Nagy, *J. Amer. Chem. Soc.* **85**, 127 (1963).

[5] B. H. Jennings and S. N. Townsend, *J. Phys. Chem.* **65**, 1574 (1961).

[6] S. C. Srivastava, *Nature, Lond.* **182**, 47 (1958).

[7] S. Prakash and S. C. Srivastava, *J. Ind. Chem. Soc.* **35**, 797 (1958).

[8] S. Prakash and S. C. Srivastava, *Z. Physik. Chemie* **208**, 127 (1957).

titanate transducer having a frequency of 1 Mc/sec. All experiments were performed at a fixed output to the crystal (R.F. output = 1·8 KV approx), except when the effect of sonic intensity was to be studied. Additional apparatus consisted of a suitable ultrasonic bath, a reaction vessel and an easy mechanism for the coupling of the reaction vessel to the transducer, details of which have been described.[9] In each experiment, a solution (20 ml) in a 250 ml Jena glass bottle was exposed. The temp was kept 28 ± 0·2°. Some results from Tables 1 and 2 are plotted in Figs. 1 and 2.

The results obtained by exposing aqueous solutions of ethyl iodide and iodobenzene to ultrasonic waves have been recorded in Tables 1, 2 and 3. In Table 4, the effect of ultrasonic intensity on the sonochemical decomposition of ethyl iodide is given. Similarly, the results obtained on irradiating aqueous solution of *o*-dichlorobenzene are incorporated in Table 5.

TABLE 1. IODOBENZENE

Time of exposure (min)	Titre value of $N/208$ $AgNO_3$ for 5 ml of soln. (I^-)	Titre value of $N/208$ Hypo after adding $KI + H_2SO_4$ (H_2O_2)	Total iodide liberated in g per mole	Zero order velocity constant $K_0 = dx/dt$	
				k_{0_I}	$k_{0_{H_2O_2}}$
5	0·22	0·10	27·4032	0·024	0·020
10	0·34	0·20	42·3504	0·028	0·020
15	0·48	0·30	59·7888	0·024	0·016
20	0·60	0·38	74·7360	0·024	0·020
25	0·72	0·48	89·6832	0·024	0·020
30	0·84	0·58	104·6304		0·024
45	0·62	0·80	77·2272		0·030
60	0·46	1·10	57·2976		
			Average =	$2·48 \times 10^{-2}$	$2·14 \times 10^{-2}$

TABLE 2. ETHYL IODIDE

Time of exposure (min)	Titre value of $N/208$ $AgNO_3$ ($I_2 + I^-$)	Titre value of $N/208$ Hypo (I_2)	Titre value of $N/208$ Hypo after adding $KI + H_2SO_4$ ($H_2O_2 + I_2$)
5	1·90	0·18	0·26
10	2·24	0·30	0·56
15	2·58	0·42	0·84
20	2·94	0·52	1·14
25	3·24	0·68	1·44
30	3·58	0·82	1·74
45	4·60	1·18	2·52
60	5·68	1·54	3·34
75	6·70	1·94	4·22
90	7·66	2·36	5·12
120	7·50	2·28	4·84
135	7·42	2·18	4·50

DISCUSSION

From the observations recorded in Tables 1, 2, 3 and 5, it is clear that iodobenzene and *o*-dichlorobenzene give halogen as hydrogen halides whereas ethyl iodide in addition liberates free halogen. The amount of hydrogen peroxide generated during

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[9] S. Prakash, A. D. Pandey and J. D. Pandey, *Talanta* **11**, 1113 (1964).

TABLE 3. EXTRAPOLATED FROM TABLE 2

Time of exposure (min)	K_O (I^-,I_2)	K_{OI_2}	K_{OI^-}	$K_{OH_2O_2}$	I_2 liberated per g mole
5					2·1702
	0·068	0·024	0·044	0·036	
10					3·6171
	0·068	0·024	0·044	0·032	
15					5·0639
	0·072	0·028	0·044	0·032	
20					6·2796
	0·060	0·024	0·036	0·036	
25					8·1987
	0·068	0·028	0·040	0·032	
30					9·8867
	0·068	0·024	0·044	0·028	
45					14·2272
	0·072	0·024	0·048	0·0306	
60					18·5677
	0·068	0·026	0·041	0·032	
75					23·3905
	0·064	0·028	0·036	0·032	
90					28·4545
120					27·4899
135					26·2842
Average values: of $K \times 10^2$	6·88	3·18	4·18	3·23	

TABLE 4. EFFECT OF INTENSITY
Time of exposure: 10 min.

R.F. Volts (KV)	Titre value of $N/210$ Hypo for 10 ml of solution (I_2)	Titre value of $N/210$ Hypo for 10 ml of solution ($H_2O_2 + I_2$)
1·5	0·12	0·24
1·7	0·36	0·68
1·9	0·88	1·52
2·0	0·96	1·64
2·1	1·10	1·86
2·2	1·24	2·12
2·3	1·48	2·28

the irradiation time was also estimated and presented in terms of titre values of sodium thiosulphate. In all cases the rate of sonocleavage follows the zero order kinetics (Figs. 1 and 2) and values of zero order velocity constants (K_O) are calculated and the average values given in the corresponding Tables. Taking the analogy of perfect photochemical reactions in which the velocity of the reaction is proportional to the intensity of light, the explanation for the zero order of the sonochemical halogen liberation may probably lie in the assumption that the rate of the reaction is proportional to the intensity of ultrasonic waves. Our experimental results also demonstrate that the amount of halogen released increases with the duration of ultrasonic exposure. The production of halogen atoms increases up to a certain time beyond which there is no further increase. After this optimum time, either it decreases (Tables 1, 2 and 3) or remains constant. In Table 4, the amount of free iodine and hydrogen peroxide liberated during the sonocleavage of ethyl iodide is given.

All chemical reactions, in the field of ultrasonic waves, are governed by cavitation which refers to the formation and collapse of small bubbles or cavities in the liquid as a result of pressure changes. Further, it should be emphasized that generally only aqueous systems support sonochemical reactions, which do not take place in pure organic liquids. This is attributed to a particular property or a combination of unique properties of water which are responsible for the abnormal high release of energy from the cavitation bubbles. A better approach to this problem has recently been made by supposing the internal pressure[10–12] and surface tension[5] of liquids to be important parameters in the sonochemical reaction. These reactions will only occur when the internal pressure of the reaction medium exceeds some critical threshold value. The effective rate of such reactions is associated with the energy of collapse of cavitational holes. Since the internal pressure of water is 3–5 times greater than that of most organic halides, such a view would qualitatively account for the sonochemical decomposition of aqueous solutions of these substances but not when they are present in a pure state and at the same time assign an appropriate rôle to the cavitational intensity. The higher the values of surface tension and internal pressure of the reaction solution the greater the amount of energy released upon collapse of the cavitation bubbles. Consequently one would expect that the solvent as well as the solute (in case of a liquid solute) would be present inside the cavitational bubbles and that on collapse of these bubbles the molecules of both the liquid vapours would

TABLE 5. *o*-DICHLOROBENZENE

Time of exposure (min)	Titre value of $N/100$ $AgNO_3$ for 10 ml of exposed solution	Zero order velocity constant $K_0 = \frac{dx}{dt}$	Amount of chlorine liberated per g mole of $C_6H_4Cl_2$
5	0·88		31·4512
		0·032	
10	1·04		37·1696
		0·036	
15	1·22		43·6028
		0·028	
20	1·36		48·6064
		0·032	
25	1·52		54·3248
		0·032	
30	1·68		60·0432
45	1·68		
60	1·68		
	Average = $3{\cdot}20 \times 10^{-2}$		

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[10] N. Berkowitz and S. C. Srivastava, *Canad. J. Chem.* **41**, 1787 (1963).

[11] N. Berkowitz and S. C. Srivastava, *Canad. J. Chem.* in press.

[12] S. Prakash and J. D. Pandey, *Chim. Analytique* in press.

undergo decomposition simultaneously. So the statement, which has been forward by a number of investigators in this field that the decomposition of water molecules is the principal cause for the decomposition of the solute while working with aqueous solutions seems to be confusing and has been explained earlier.[12] Thus one may conclude that in the sonochemical decompositions of aqueous solutions of ethyl iodide, iodobenzene and *o*-dichlorobenzene, two primary reactions take place simultaneously.

$$H\cdot OH \rightarrow H + OH \qquad E = 120\,\mathrm{Kcal}$$

$$OH + \mathrm{Org.\ Halides} \rightarrow \mathrm{Products}$$

As far as the sonochemical decomposition of water is concerned, a number of free radical mechanisms have been proposed.[13–15] The main result of sonolysis of water is the formation of H and OH radicals. The formation of hydrogen peroxide during irradiation takes place as follows:

$$2OH \rightleftharpoons H_2O_2$$

In oxygenated solutions, additional H_2O_2 may be formed by the following route.

$$H + O_2 \rightarrow HO_2$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

Considering the above facts, the probable free radical mechanism for the liberation of halogen atoms from aqueous solutions of (1) C_2H_5I, (2) C_6H_5I and (3) $C_6H_4Cl_2$ may be formulated as follows:

$$C_2H_5I \rightarrow C_2H_5 + I \qquad E = 45{\cdot}0\,\mathrm{Kcal} \tag{1}$$

In comparison to C—CI and C—Br bonds, the C—I bond is weaker and it may easily be broken by the available ultrasonic energy.

$$C_2H_5I + 2H \rightarrow C_2H_6 + HI$$

$$C_2H_5 + H \rightarrow C_2H_6$$

$$C_2H_5I + OH \rightarrow C_2H_4 + H_2O + I$$

$$\rightarrow C_2H_5(OH) + I$$

$$H + I \rightarrow HI$$

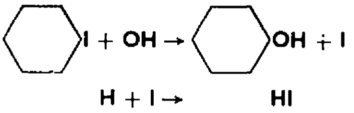
$$I + I \rightarrow I_2$$

$$H + H \rightarrow H_2$$

The activated oxygen produced may oxidize the alcohol to aldehyde.

$$C_2H_5OH + O \rightarrow CH_3CHO + H_2O$$

$$CH_3CHO + O \rightarrow CH_3COOH$$

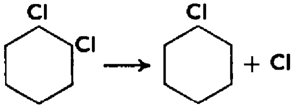


(2)

The formation of acetylene and diacetylene has been shown by various workers.[2-4] Both iodobenzene and phenol or either of the two separately depolymerize or decompose (caused by cavitation) to give the products as follows:

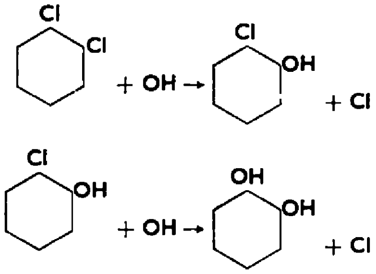
$$C_6H_5I \rightarrow CH{\equiv}C{-}C{\equiv}CH + CH{\equiv}CH + HI$$

$$C_6H_5OH \rightarrow CH{\equiv}C{-}C{\equiv}CH + CH{\equiv}CH + H_2O$$



(3)

Dichlorobenzene may further react under the action of ultrasonic waves forming chlorophenol, HCl and catechol



$$H + Cl \rightarrow HCl$$

The other radicals may combine likewise. The chlorobenzene, phenol or directly the *o*-dichlorobenzene would further depolymerize yielding acetylene and diacetylene.

$$C_6H_4Cl_2 \rightarrow CH{\equiv}C{-}C{\equiv}CH + CH{\equiv}CH + 2Cl$$

$$C_6H_5Cl \rightarrow CH{\equiv}C{-}C{\equiv}CH + CH{\equiv}CH + HCl$$

$$C_6H_5OH \rightarrow CH{\equiv}C{-}C{\equiv}CH + CH{\equiv}CH + H_2O$$