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Medium Effect on the Sonochemical Decomposition of Tribromomethane

R. G. Makitra[a], G. G. Midyana[a], and E. Ya. Pal'chikova[b]

[a] *Fossil Fuel Branch, Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, ul. Nauchnaya 3a, Lviv, 79060 Ukraine*
e-mail: gmidyana@gmail.com

[b] *Institute of Geology and Geochemistry of Fossil Fuels, National Academy of Sciences of Ukraine, Lviv, Ukraine*

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Abstract—The amount of bromine released at the sonochemical decomposition of bromoform in the presence of organic solvents depends on the ability of the latter to specific solvation.

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The ultrasound is an efficient factor promoting a number of chemical reactions, including oxidation of organic substrates [1]. At the same time, a number of organic solvents retard or even suppress the chemical processes taking place under the influence of ultrasound. Since this inhibitory effect is particularly noticeable in the presence of low-boiling solvents with high vapor pressure, it is commonly assumed that the inhibition is associated with the destruction of cavitation bubbles. However, the nature of this phenomenon is still not completely clear, and a number of works suggest that other factors may influence the process.

The effect of organic solvent additives of different nature on the decomposition of tribromomethane (bromoform) proceeding with release of elemental bromine in the aquatic environment under the influence of ultrasound was studied in [2]. In the experiments 20 ml of saturated aqueous $CHBr_3$ solution (0.9938 g/100 ml) was taken to which was added 4 ml of distilled water and 1 ml of organic solvent. The sample was placed in a glass reactor, irradiated with ultrasound of the frequency of 1 megacycle per second and power of 375 W. Fandey et al. suggest that the liberated bromine reacts with the added organic liquid to form a relatively stable halo derivative, which, in turn, partially decomposes under the influence of ultrasonic irradiation releasing the elemental bromine. The total amount of free bromine was determined by volumetric analysis.

The table lists the total amount of free bromine Q (gram per 1 mol of solvent) separated in 5 min at the irradiation. As can be seen, depending on the nature of the added organic liquid, the amount of bromine may vary within one order of magnitude as compared with water. However, in [2] Fandey et al. failed to find a quantitative relationship between the yield of bromine Q in g per 1 mole of organic additive. To understand these differences they suggested a number of causes on the basis of analysis of published data, in particular, the influence of viscosity, surface tension or the medium polarity, varied under the influence of organic additives. Thus, it is known that the higher viscosity of a fluid, the greater would be the cavitation threshold of the cavitation bubble growth and, consequently, the faster the sonochemical process. Indeed, in the presence of associated viscous liquids like ethylene glycol, glycerol, and diethylene glycol the process is decelerated, but the deceleration is even more noticeable in the presence of low-viscous liquids such as methanol, acetone, and benzene. On the contrary, the greater the surface tension of the liquid, the greater the energy released at the collapse of the cavitation bubbles and the greater the rate and efficiency of the sonochemical reaction. However, the distinct dependence of log Q on the surface tension of the additive is absent (Fig. 1). Here we do not consider the questionable assumption that the addition of ~4% of the solvent can alter substantially the properties of the water environment, and that some of additives (hydrocarbons, chloroform) are virtually insoluble in

Yield of bromine Q at the sonochemical decay of bromoform per 1 mol of organic solvents by data of [2], experimental values of surface tension σ at 20°C, the Hildebrand parameter square δ^2, and the values of log Q calculated with Eq. (3)

Run no.	Solvent	σ, dyn cm^{-1}	δ^2, kJ mol^{-1}	Q, g	log Q		
					experimental	calculated	Δlog Q
1	Benzene	28.85	349.7	2.65	0.4232	0.5098	0.0866
2	*m*-Xylene	28.90	320.4	7.95	0.9004	0.8110	–0.0894
3	Chloroform	27.14	353.1	26.52	1.4236	0.3389	–1.0846
4	Methanol	23.00	876.2	14.58	1.1638	1.2969	0.1331
5	Ethanol	20.00	676.0	22.01	1.3426	1.2004	–0.1422
6	*n*-Butanol	24.60	542.9	23.60	1.3729	1.3751	0.0022
7	Ethylene glycol	47.70	868.3	21.21	1.3265	1.2457	–0.0808
8	Diethylene glycol	–	612.9	24.66	1.3920	1.4899	0.0979
9	Glycerol	63.40	1200.0	23.07	1.3630	1.3751	0.0121
10	Dioxane	35.42	408.0	13.26	1.1225	1.1229	0.0004
11	Acetone	23.70	397.2	3.98	0.5999	0.6126	0.0127
12	Water	73.03	2290.0	29.17	1.4649	1.4325	–0.0324

water and will likely extract $CHBr_3$ into the organic phase.

The foregoing leads to an assumption that the process studied in [2] depends complicatedly on the properties of the organic component of the system. Such reactions can be described on the basis of the principle of linearity of free energies (FEL) by linear multiparameter equations taking into account the different characteristics of the organic phase [3]. Also, by this way it is possible also to generalize the influence of additives of organic liquids to water. For instance, in [4] the data on the solubility of lithium carbonate in five binary aqueous-organic mixtures were similarly processed.

It is presumable that the process of the substrate decay to liberate bromine is carried out in the $CHBr_3$–

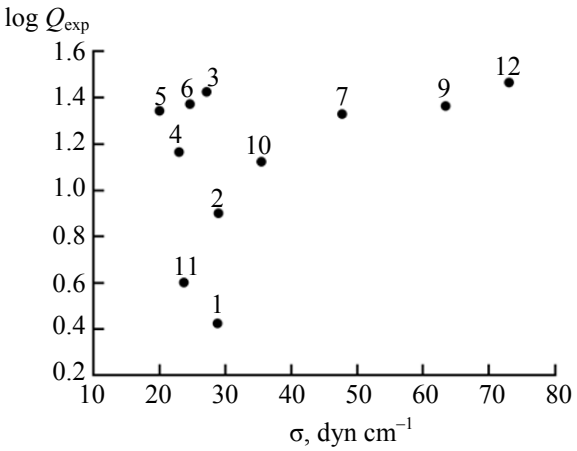

Fig. 1. Yield of bromine Q at sonochemical decay of bromoform in the presence of 1 mol of organic solvents vs. surface tension σ of the solvents. Numbers of points correspond to the table.

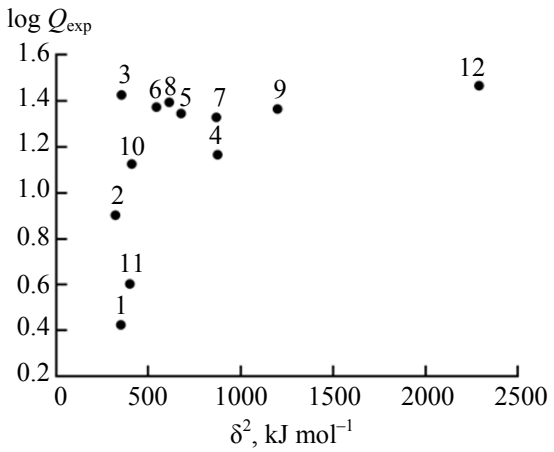

Fig. 2. Yield of bromine Q at sonochemical decay of bromoform in the presence of 1 mol of organic solvents vs. the square of Hildebrand parameter δ^2 of the solvents. Numbers of points correspond to the table.

organic solvent microassociates. Since the yield of bromine Q depends on the rate constant of its formation, in accordance with the principle of FEL we used log Q as generalized values. The calculation was carried out in accordance with [3], with the six-parameter Eq. (1):

$$\log Q = a_0 + a_1 f(n^2) + a_2 f(\varepsilon) + a_3 B + a_4 E_T + a_5 \delta^2 + a_6 V_{M.} \quad (1)$$

In (1) n and ε are respectively the refractive index and the dielectric constant of organic component that determine its polarity and polarizability. The basicity B according to Palm, and the electrophilicity E_T according to Reihardt characterize its ability to specific solvation, the square of Hildebrand solubility parameter δ is proportional to the energy of self-association (cohesion) of the liquid, and V_M is its molar volume.

Treatment of the data for all 12 solvents led to an expression with an unacceptably low value of the multiple correlation coefficient, R = 0.7369. However, after excluding from the consideration the most deviating data for chloroform (possibly due to its extremely low solubility in water) an equation was obtained that adequately generalizes the experimental data:

$$\log Q = -0.6388 - (4.7549\pm1.6858) f(n^2) - (3.6286\pm0.8064) f(\varepsilon) + (0.0021\pm0.0006) B + (0.0652\pm0.0130) E_T + (0.0001\pm0.0001)\delta^2 + (0.0112 \pm 0.0024) V_M. \quad (2)$$

With R = 0.9720 and standard error s = ± 0.0818; maximum pair correlation coefficients r for log Q occur with E_T 0.7826 and 0.6829 In. After eliminating insignificant member containing δ^2 a five-parameter equation with R = 0.9703 was obtained, and further exclusion of relatively minor term $f(n^2)$ also results in an adequate four-parameter Eq. (3).

$$\log Q = -1.2266 - (2.8324\pm0.7929) f(\varepsilon) + (0.0023\pm0.0007) B + (0.0558\pm0.0096) E_T + (0.0051\pm0.0019) V_{M,}$$
$$R\ 0.9436;\ s\ 0.1153. \quad (3)$$

The table lists the experimental data of log Q, those calculated with Eq. (3), and their difference, Δlog Q. As can be seen, the analysis of signs in the Eqs. (2) and (3) suggests that specific solvation of the $CHBr_3$ molecule favors its decay: Obviously a weakening occurs of the C–Br bonds as a result of nucleophilic solvation of the electron-deficient hydrogen atom and electrophilic solvation of the bromine atoms. At the same time, the nonspecific solvation, especially by the more polar solvents, stabilizes the original molecule. It should be emphasized that, contrary to some suggestions, the self-association of organic solvents does not affect the process of sonochemical decay of $CHBr_3$ (Fig. 2).

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