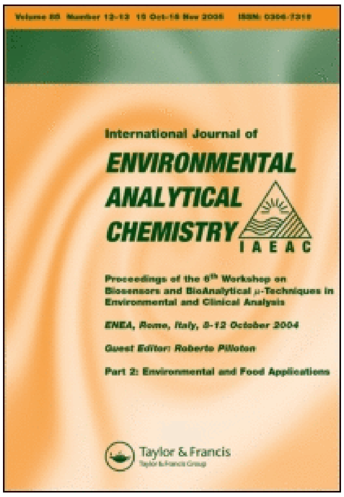

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REDOX TRANSFORMATION OF SOME AQUEOUS ORGANIC COMPOUNDS UNDER STATIC SONOLYSIS

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Ultrasound was applied to low molecular weight organic compounds in dilute aqueous solutions. The transformation of these dilute methanol, acetone, formaldehyde and acetaldehyde solutions under static sonolysis at ambient condition was found to form acetate and formate products, which were measured by ion chromatography. These chromatograms were deduced from the ion chromatograms of known standards prior to and after the sonolysis of the sample runs.

Under static sonolysis, the dilute methanol solutions yielded more acetate than formate and the formaldehyde solutions also produced a substantial amount of acetate besides the formate product. The redox transformation mechanism of the one carbon compounds as CH_3OH and HCHO solutions to form the two carbon containing acetate product was presented.

KEY WORDS: Redox transformation, static sonolysis, aqueous organics.

INTRODUCTION

The sonolysis process is selected because the degradation of organic compounds occurs near ambient condition and in the absence of added chemicals.[1-3] This work applied ultrasound to low molecular weight organic compounds in dilute aqueous solutions to form ionic products, which are potentially as removable by ion-exchange resins. The underlying reason is to provide potable water for future manned space missions. The ultrasonic chemical decomposition of aqueous organic solutions is caused by cavitation phenomenon which creates, enlarges and implodes bubbles in the liquid.[4] The implosion temperatures of these collapsing cavities reach thousands of degree Kelvin and pressures to hundreds atmospheres in a microsecond.[5] These local hot spots dissociate the water molecules into hydrogen atoms and hydroxyl radicals, which produce a wide range of redox transformation reactions in the solutions. For a sense of scale of ultrasonic irradiation of water with an immersion horn at about 50 Wcm^{-2}, the rate of peroxide formation is 10 to 50 $\mu Mmin^{-1}$.[6]

Power ultrasound at 20 kHz was reported to degrade aqueous 1,1,1-trichloroethane (i.e., suspended, dissolved or present in separate phase) under ambient condition into ionic species,[1,7] which were removable by ion-exchange resins and the volatiles by ultrasonic degassing.[3] The ultrasonic digestion and degassing process was reported to reduce about half of the organics in a radioactive discharge stream of a nuclear power plant, after the sonicated effluent had been passed through the ion-exchange resin columns.[8] The coupled technology of ultrasound and ultraviolet light had also been applied to the decomposition of aqueous 1,1,1-trichloroethane,[7] ethylene glycol and urea, [9] and the degradations of the ion-exchange resins (for resin-leakage detections by means of ion chromatography) in the water stream of a nuclear power plant.[10,11]

EXPERIMENTAL

The sonicator (Model W-385 with an average output power of 475 watts, 20 kHz frequency and 125 Wcm^{-1} intensity) and its cuphorn attachment (Model 431A) were purchased from Heat Systems Ultrasonics. Its titanium horn surface (5 cm diameter) was submerged in the circulating cold water bath inside the horn cup. This arrangement allows an easy way to sonicate several screw-capped tube samples (polypropylene screw-capped borosilicate glass tube, 13 mm OD and 100 mm height, purchased from Fisher, containing 4 ml aqueous solution under atmospheric air or argon atmosphere) at 1.5 mm above the titanium horn's radiating surface. Sonolysis took place inside the capped tubes without probe intrusion and under selected atmospheric gas and controlled temperature by the circulating bath water. The sonolysis time was 30 minutes.

Anhydrous methanol (99.8+%) was purchased from Mallinckrodt, acetone (99.5+%) from EM Science and formaldehyde (37% in H_2O, ACS) and acetaldehyde (99.5+%) from Johnson Matthey Electronics. These organic reagents, which were analyzed by gas chromatograph/mass spectrometry (Hewlett-Packard 5890/5970B quadrupole) or gas chromatograph (Hewlett-Packard 5880A) with the flame ionization detector, were equivalent to or of better qualities than the labelled grades and were used as received. The aqueous organic samples were prepared with doubly deionized 18.2 megohm-cm water, which was also analyzed by the total organic carbon (TOC) analyzer (O.I. Model 700) to assure the absence of trace organics at ppb level. The pure argon gas (99.9995+%) was purchased from Matheson. The acetate and formate products were measured by ion chromatography (Dionex 4000i), whose detection limits are at the level of 0.1 µg/l. The concentrations of formate and acetate products were quantified by known standard concentrations (e.g., an aqueous solution containing a mixture of 1.0 mg/l formate and 1.0 mg/l acetate anions in 18.2 megohm-cm water, which had also been confirmed to be absent of trace organics by TOC analyzer before standard preparation).

RESULTS AND DISCUSSION

Figure 1 shows the ultrasonic effect of aqueous methanol and acetone. The acetate and formate products were measured by ion chromatography and their concentrations were estimated from the ion chromatograms of known standards. The formate anion was not

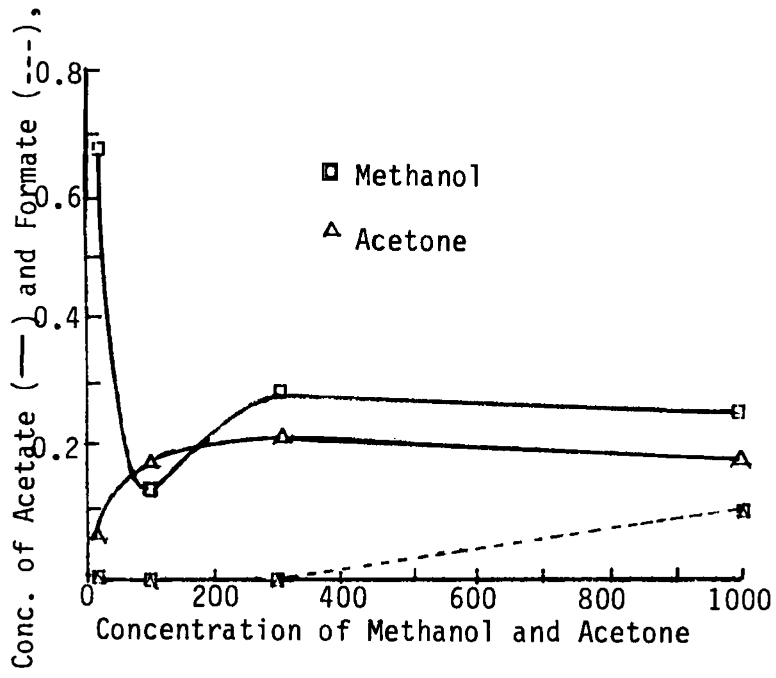

Figure 1 Ultrasonic production of acetate and formate from aqueous methanol and acetone. Concentrations in mg/l.

observed for methanol and acetone solutions below 300 ppm. Figure 2 depicts the percent destruction versus concentration of aqueous methanol and acetone after 30 minutes of sonolysis time in accordance with equations (1) and (2) respectively:

$$\%\ \text{Destruction of } CH_3OH = \frac{(2\times \text{Conc Acetate} + \text{Conc. Formate}) \times 100}{\text{Conc. } CH_3\,OH} \tag{1}$$

where one acetate anion designates the source from two methanol molecules.

$$\%\ \text{Destruction of } CH_3\,COCH_3 = \frac{(\tfrac{2}{3}\ \text{Conc Acetate} + \tfrac{1}{3}\ \text{Conc. Formate}) \times 100}{\text{Conc. } CH_3\,COCH_3} \tag{2}$$

where one acetate anion designates the source from 2/3 of the acetone molecule and one formate anion from 1/3 of the acetone molecule. The percent destructions reached 60% at 3 mg/l based on the acetate anion. No formate was detected at 3 mg/l for either methanol or acetone.

Both formaldehyde and acetaldehyde solutions produced formate and acetate anions after 30 minutes of sonolysis, except formaldehyde produced more formate anion than acetate and acetaldehyde produced more acetate anion than formate (Figure 3) A continued presence of acetate anion was observed as the concentration of formaldehyde decreased below 100

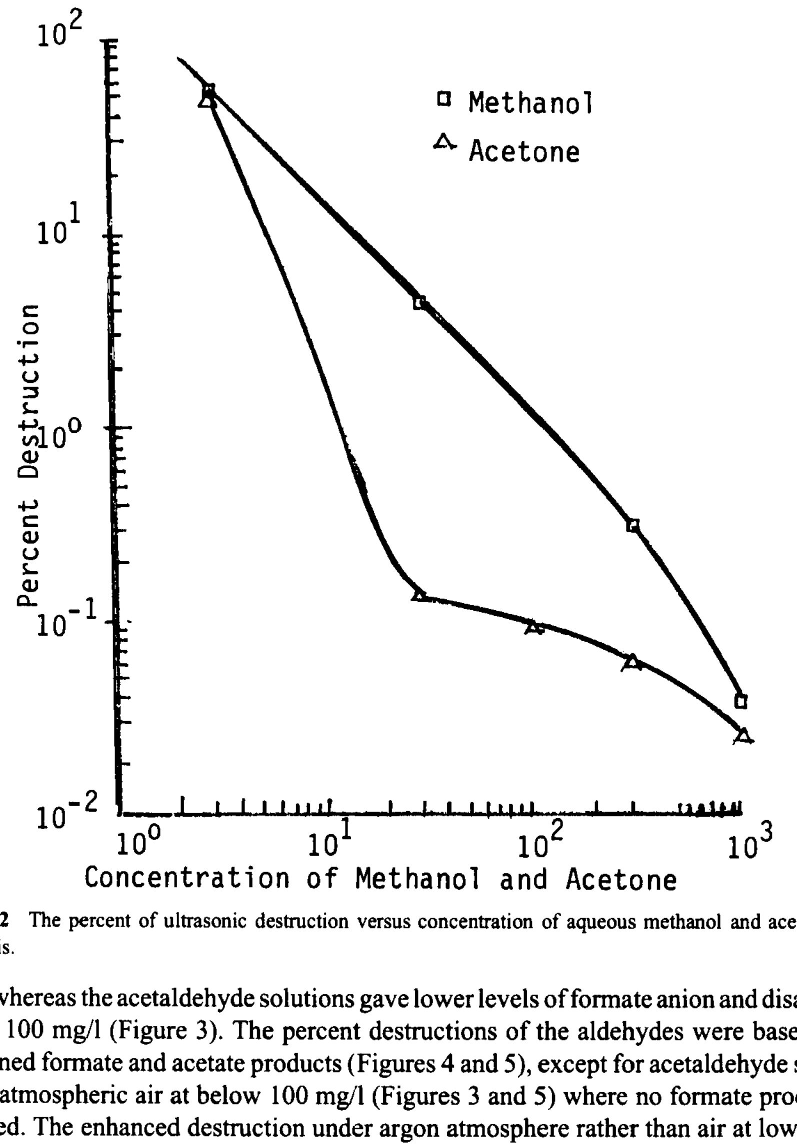

Figure 2 The percent of ultrasonic destruction versus concentration of aqueous methanol and acetone under sonolysis.

mg/l, whereas the acetaldehyde solutions gave lower levels of formate anion and disappeared below 100 mg/l (Figure 3). The percent destructions of the aldehydes were based on the combined formate and acetate products (Figures 4 and 5), except for acetaldehyde solutions under atmospheric air at below 100 mg/l (Figures 3 and 5) where no formate product was detected. The enhanced destruction under argon atmosphere rather than air at low concentrations can be explained by further breaking down of acetate and formate (e.g., at 3 mg/l) and thus the calculated % destructions appear less (as a possible error source). The other explanation is that the higher implosion temperatures under the monoatomic gas as argon than the diatomic gas as air have been reported[12] and argon also possesses lower thermal conductivity than air to retain the heat of collapsing cavity longer than air. In Figure 4 the percent destruction of formaldehyde was estimated by equation (3):

$$\%\ \text{Destruction of HCHO} = \frac{(2 \times \text{Conc Acetate} + \text{Conc. Formate}) \times 100}{\text{Conc. HCHO}} \qquad (3)$$

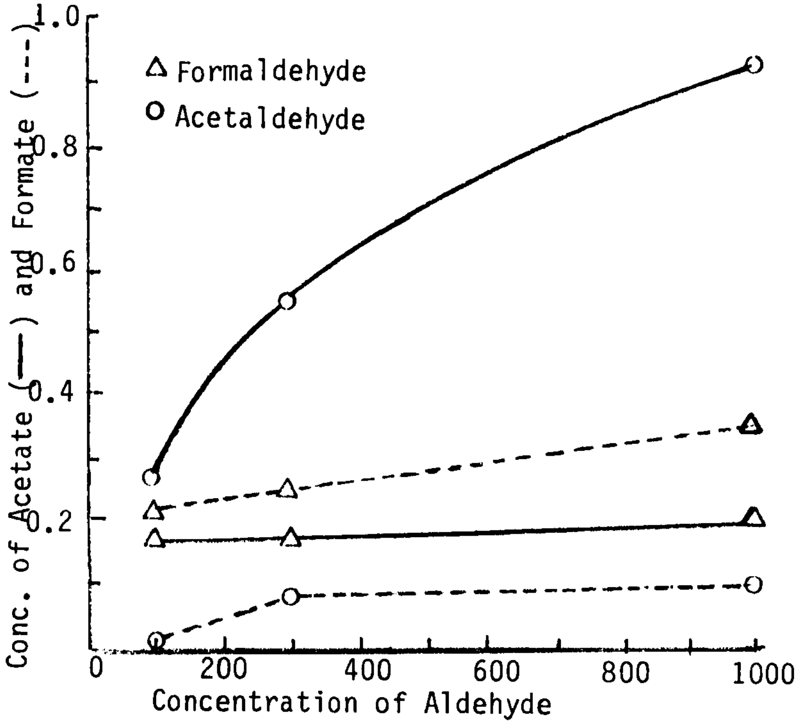

Figure 3 Ultrasonic production of acetate and formate from aqueous formaldehyde and acetaldehyde solutions. Concentrations in mg/l.

where one acetate anion designates the source from two formaldehyde molecules. In Figure 5, the percent destruction of acetaldehyde was calculated by equation (4):

$$\%\ \text{Destruction of } CH_3CHO = \frac{(\text{Conc Acetate} + \frac{1}{2}\,\text{Conc. Formate}) \times 100}{\text{Conc. } CH_3CHO} \qquad (4)$$

where one formate anion containing one carbon atom is equivalent to half of the two carbon-containing acetaldehyde molecule.

It is of interest to note here that at 100 mg/l (Figure 3) the one carbon containing formaldehyde molecule produces a substantial amount of the two carbon-containing acetate anion. Figure 1 also shows that the one carbon-containing methanol produces mainly acetate anion at 100 mg/l. This transformation pattern of sonolysis under static condition is unlike the usual changes of organic compounds in dilute solutions. The redox transformation mechanism of these two organic compounds (HCHO and CH_3OH) is believed to be related, since methanol readily oxidizes to formaldehyde and oxidation is known as the most common result in sonicated aqueous solutions. A head-to-head coupled formaldehyde is postulated as one of the key intermediates (-OCH_2CH_2O-or-CH_2CH_2OO-). This dimeric

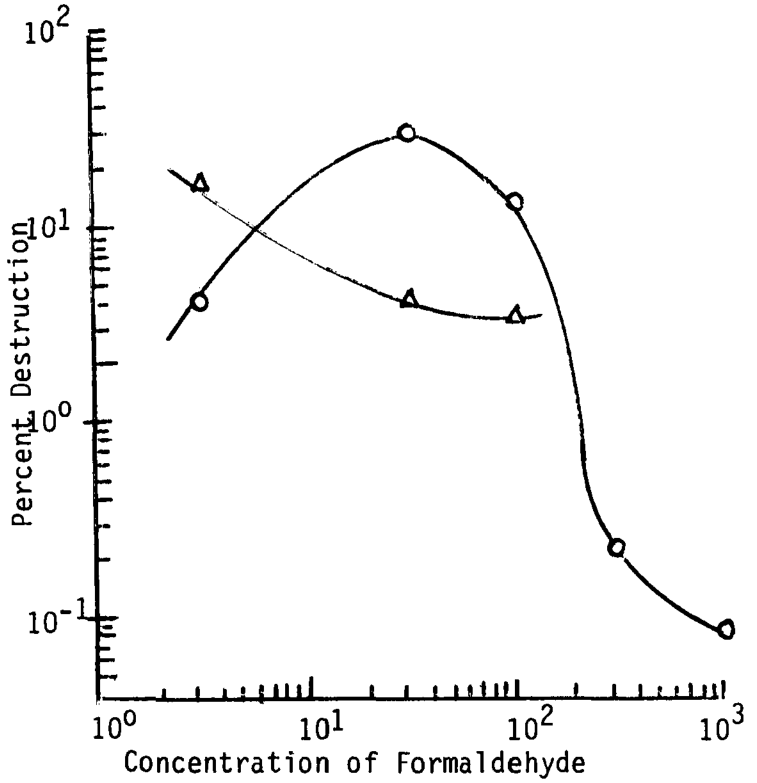

Figure 4 The percent of ultrasonic destruction versus concentration (in mg/l) of aqueous formaldehyde under 1 atm of air O and pure argon △.

intermediate rearranged its one hydrogen atom by hydrogen abstraction or shift from one carbon to the other neighboring carbon under redox environment. This caused the reduction of one carbon and oxidation of the other. This path formed acetate anion product. The other randomly coupled head-to-tail formaldehyde intermediate ($-CH_2O-CH_2O-$) is postulated to rearrange and hydrolyze under the redox mode. This path formed two products: the oxidized formate and the reduced methanol, which is oxidizable to formaldehyde and thus the dimeric head-to-head intermediate is favored for the overall process. This head-to-head dimer intermediate supports the predominant acetate anion product under static sonolysis.

CONCLUSION

The transformation of dilute aqueous methanol, acetone, formaldehyde and acetaldehyde solutions was found to form acetate and formate products under static sonolysis at ambient conditions. The redox transformation mechanism of one carbon compounds as CH_3OH and

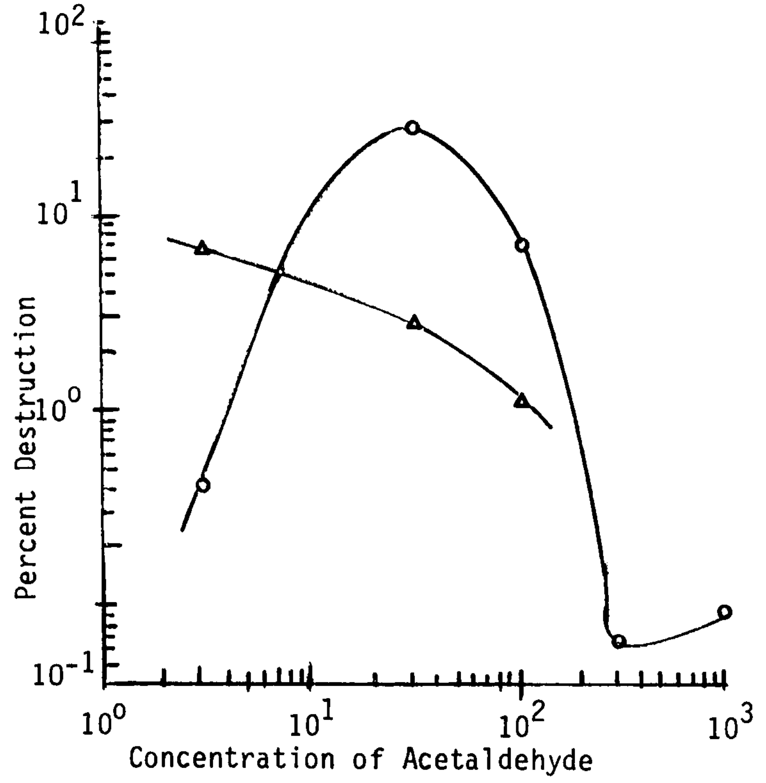

Figure 5 The percent of ultrasonic destruction versus concentration (in mg/l) of aqueous acetaldehyde under 1 atm of air O and pure argon △.

HCHO solutions to form the two carbon containing acetate product was concluded from the same dimeric intermediate, which is a head-to-head coupled formaldehyde prior to its rearrangement into the acetate product under the redox environment.

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