

OC-2: Effect of Ultrasonic Frequency on the Mechanism of Formic Acid Sonolysis

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The kinetics and mechanism of formic acid sonochemical degradation were studied at ultrasonic frequencies of 20, 200 and 607 kHz under argon atmosphere. Total yield of HCOOH sonochemical degradation increased approximately 6-8 fold when the frequency increased from 20 to 200 or to 607 kHz. At low ultrasonic frequencies, HCOOH degradation has been attributed to oxidation with OH• radicals from water sonolysis, and to HCOOH decarboxylation occurring at the cavitation bubble-liquid interface. With high-frequency ultrasound, the sonochemical reaction is also influenced by HCOOH dehydration. Whatever the ultrasonic frequency, the sonolysis of HCOOH yielded H₂ and CO₂ in the gas phase as well as trace amounts of oxalic acid and formaldehyde in the liquid phase. On the other hand, CO and CH₄ formations were only detected under high-frequency ultrasound as shown in Figure 1.

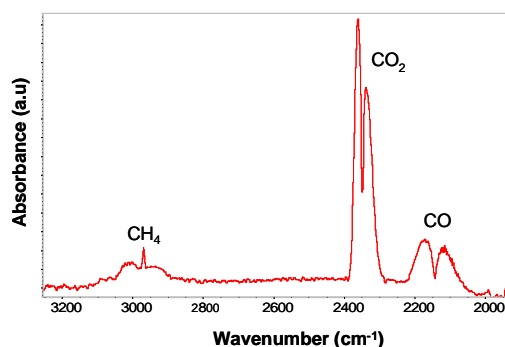


Figure 1: IR-spectrum of the outlet gas obtained after 1 hour of 3M HCOOH sonolysis, 20°C, 200 kHz, argon.

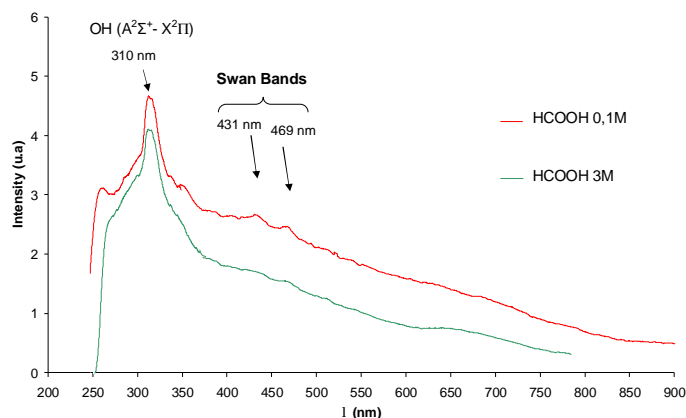


Figure 2: Sonoluminescence spectra obtained during sonolysis of acid formic solutions (Argon, 607 kHz, 20°C, 0.26 W mL⁻¹)

The most striking difference between low-frequency and high-frequency ultrasound is that the sonolysis of HCOOH at high ultrasonic frequencies initiates Fischer-Tropsch hydrogenation of carbon monoxide leading to the formation of CH₄. Moreover, sonoluminescence experiments at high frequency ultrasound show the emission bands at 431 and 469 nm corresponding to the transitions $d^3\Pi_g \rightarrow d^3\Pi_u$ of excited C₂* molecules, also called Swan Bands (Flint and Suslick, 1989). As shown in Figure 2, the intensities of these bands are very weak and are the same whatever the HCOOH concentration, which shows that formic acid degradation occurs at the cavitation bubble-liquid interface even at 3 M. The formation of C₂* species is probably due to the presence of CO inside the bubble cavitation and not to CO₂ which quenches the sonoluminescence.

Reference

Flint, E. B., Suslick, K. S. 1989, Sonoluminescence from Nonaqueous Liquids: Emission from Small Molecules J. Am. Chem. Soc. 1989, 111, 6987-6992.