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Perfluorocarbons as Inert Gases in Homogeneous Sonochemistry

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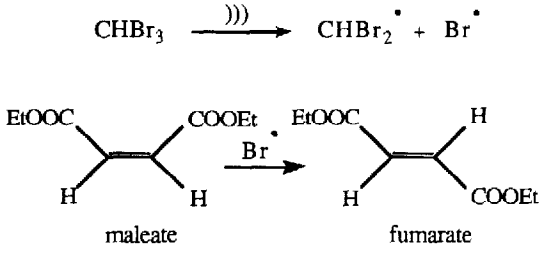
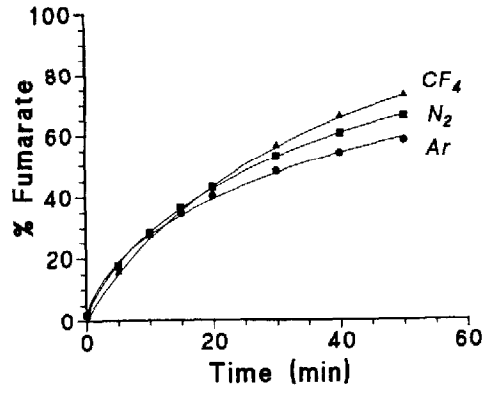
Abstract. *The polyatomic inert gases CF_4 and C_2F_6 are efficient in homogeneous sonochemistry. This observation leads to the conclusion that some analogies could exist between sonochemistry and plasma chemistry*

Cavitation plays a central role in sonochemistry[1]. According to the hot-spot theory[2], the temperature reached during the adiabatic collapse of the cavitation bubble is higher than 13,000 K when the bubble is filled with Ar, but only 4,700 K if it is filled by C_2H_6. The reason for this difference is due to the absence of internal degrees of freedom in the case of Ar. Still according to the hot-spot theory, even in the case of a non-adiabatic collapse[3], monoatomic or possibly diatomic gases lead to higher temperatures than polyatomic gases. Suslick et al.[4,5] have accumulated experimental observations which, from their point of view, are fully in accord with the hot-spot theory, which remains without doubt the most popular theoretical model used by sonochemist[1,6,7]. Nevertheless, it must be pointed out that Margulis[8] has recently developed an electrical theory in which sonochemistry and sonoluminescence are explained by the presence of a very high transient electrical field during the bubble collapse. This collapse is described as a fragmentation process. Margulis et al.[9] have also accumulated experimental facts which, from their point of view, remain strong evidence against the hot-spot theory and in favour of the electrical theory describing phenomena which can lead to a plasma in the collapsing bubble.

In the present work we study the isomerization of diethyl maleate into diethyl fumarate (see figure) in the presence of $CHBr_3$ and under ultrasonic irradiation (frequency : 20 kHz; power measured by calorimetry 10W; steel immersion horn system from Undatim Ultrasonics ; 30 ml vessel ; temperature : 10°C ± 1°C ; solvent : CCl_4; initial $CHBr_3$ concentration : 0.38 mol l^{-1}). No isomerization has been observed either in the absence of ultrasound or in the absence of $CHBr_3$[10].

The graph shows a comparison between Ar, N_2 and CF_4. It appears clearly that CF_4 is as efficient as the other two gases and even with C_2F_6 the reaction yield is 43% after 50 minutes. In all the cases the solvent was saturated with the gas prior to the reaction, and an atmosphere of the gas was maintained over the solution during all the reaction time.





We have shown previously that carbon dioxide and xenon are much less efficient than argon and nitrogen[10]. Tetrafluoromethane and C_2F_6 are therefore better than Xe and CO_2, even if the polytropic ratios ($\gamma = C_p/C_v$) of these perfluorocarbons are obviously smaller than those of Xe or CO_2. It must be observed that the comparison between CF_4 and Ar is particularly interesting because their solubilities in CCl_4 and heat conductivities are very similar[11].

We can thus conclude that the role of γ as one of the most important properties of cavitation gas has probably been overemphasized.

It must be added that CF_4 was tested because it is known to be a very efficient gas in plasma chemistry[12]. The results reported here can be more easily explained by the electrical theory thant by the hot-spot theory.

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