

Proposal for Predictive Rules in Sonochemistry

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Abstract

From the very beginning of the study of sonochemistry the question has been asked – are there any rules which govern sonochemical reactions and if so can we predict which reactions will be most affected by ultrasonic irradiation.

This is a very deep question and so far there has been no truly satisfactory answer to it. Of course practical guidance for the laboratory use of ultrasonic energy has been around for many years [1]. These include such factors as the optimum vessel position in an ultrasonic cleaning bath or how to use an ultrasonic probe correctly. Attempts were made in those days and since to explore important aspects of the “new” science such as how to determine and report the real acoustic power entering into a system or how to measure the real temperature inside the reaction mixture. Up to now no definitive, or perhaps more correctly universally accepted, answers to these two questions have been forthcoming.

So, is there any clue as to what type of reactions are susceptible to sonication? It was proposed some years ago that sonication promotes reactions that involve electron transfer (ET), while ionic reactions are essentially insensitive to cavitation phenomena [2, 3]. In the case of an ET mechanism there are two possible pathways (see Figure 1):

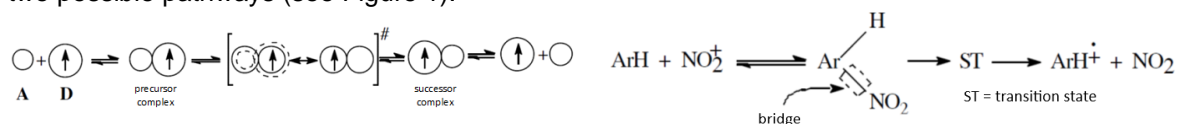


Figure 1: a) schematic model of *outer-sphere* electron transfer, b) *inner-sphere* electron transfer

It is our vision that that if a chemical reaction occurs via electron transfer then this may indeed be a candidate for true sonochemical activation. If not although the actual chemical mechanism of the reaction may be insensitive to ultrasound it will nevertheless be accelerated by the mechanical results of acoustic cavitation such as efficient mixing and jetting.

In general, sonochemical acceleration could occur for any outer-sphere transfer reaction but it is also possible, for sonochemistry to cause a sonochemical switch through an inner-sphere electron transfer reaction (e.g. [4]).

It is our suggestion that electron transfer can be facilitated during the compression phase of an acoustic wave. This compression could produce transient solid-like structures within the solution. Such structures would result in an “ordering effect” of the molecules in which electrical charges could develop. The electrical charges could facilitate electron movement from one molecule to another thereby triggering chemical reactions. Such reactions could occur even in the absence of cavitation especially if the solvent or reagents employed show piezoelectric/electrostriction properties. Similar transient ordering effects could be induced by the shockwave accompanying bubble collapse and both of these would help to explain some of the anomalous results observed in sonochemistry [5].

References

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