

ORGANIC SONOCHEMISTRY : A NEW INTERPRETATION AND ITS CONSEQUENCES

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Abstract : A rational approach of sonochemical reactions is proposed on the basis of their mechanisms. It appears that reactions which can be modified in their rate or nature of products, by ultrasound irradiation, correspond to those which proceed, at least in part, through radical intermediates.

Since its beginning, sonochemistry has been considered to take its origin in the general phenomenon of cavitation, which generates high temperatures and pressures, shock waves and particle accelerations¹. Explanations of the chemical reactivity under these conditions however seems incomplete, as finding new applications is still largely a matter of empirism. We wish to propose here a new interpretation leading to a new theoretical understanding, with a satisfactory degree of predictive value.

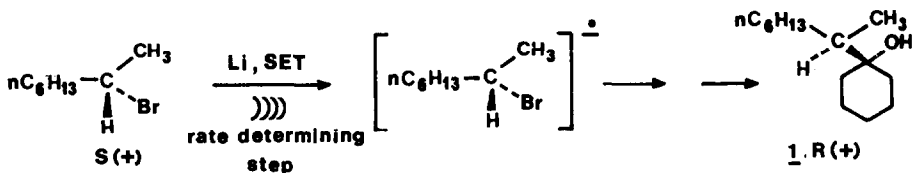
Homogeneous reactions have been studied for a long time¹⁻³. They provide the fundamental information that the reaction takes place in the collapsing cavitation bubble and in the superheated (ca 2000 K) liquid shell around it (hot spot theory⁴). Species with a sufficient vapor pressure diffuse into the cavity where they undergo the effects of the adiabatic collapse. Coordinatively unsaturated species or free radicals⁵⁻⁸ are thus generated by cavitation. These reactions correspond to a first type of sonochemical processes.

This commonly accepted theory is however incomplete and applies with much difficulty to systems involving non-volatile substances, for example solid reagents (sugars, metals...). Examination of some of these cases leads to the following considerations.

For heterogeneous systems, a second type of sonochemical processes is found for which only the mechanical effects of sonic waves are operative. In particular this is the case of sugar ketalisations⁹ or ester hydrolysis¹⁰. In this latter example, when comparing the silent and sonicated reactions, it can be noted that the reaction conducted in an homogeneous solution is only modestly accelerated (15%) while its heterogeneous analogue undergoes a much more striking effect. In all these cases, the products resulting from the silent and ultrasonic reactions are the same. No chemical mechanistic differences exist between the two processes, and the reactive ionic intermediate is not generated by cavitation.

Many heterogeneous sonochemical reactions were till recently interpreted only by the mechanical effects (agitation, or "cleaning" of a solid surface). Analysis however leads to substantial corrections. Our initial reasoning was based on the results obtained for the

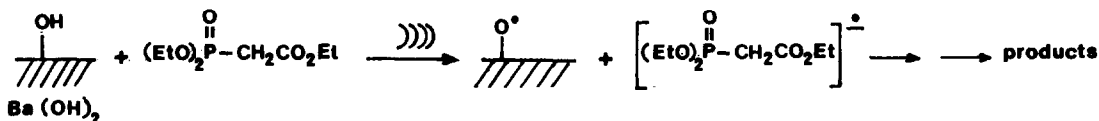
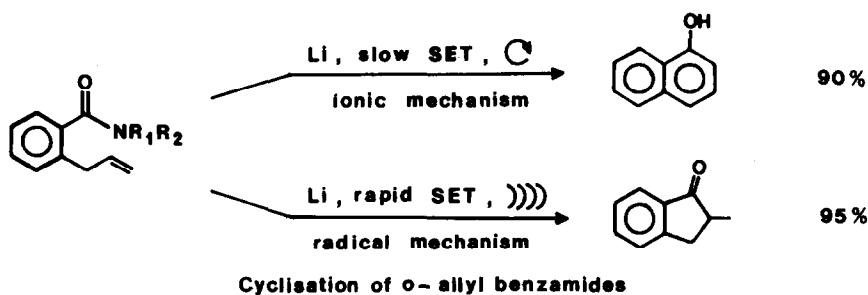
Barbier reaction¹¹. Surface activation¹² is unable to explain all the experimental observations and we established that the single electron transfer (SET) from the metal to the carbon halogen bond is stimulated by sonication (Scheme 1). This deduction is corroborated by experiments run with optically active alkyl halides¹³.



Scheme 1: e. e. of 1 increases with cavitational energy

We then envisaged that such a deduction could be extended to cases which do not involve metals, and we were led to formulate the hypothesis that the "true" sonochemical reactions (type 3) are those in which a single electron transfer is involved in a key step. Another formulation is : sonication promotes electron transfers, while ionic processes are essentially insensitive to cavitational phenomena.

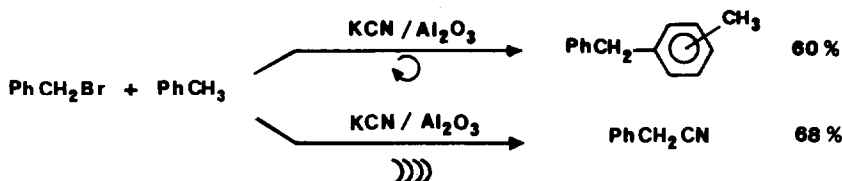
This statement is in agreement with the prediction made by Chanon, some years ago, according to which sonication should be able to modify significantly electron transfer processes¹⁴. Numerous examples in favour of this hypothesis can be found for various domains (not only organometallics) of organic chemistry. In this first approach of a new interpretation, an exhaustive list cannot be given, but the rule holds in all the cases examined till now, among which can be cited : the cyclisation of o-allylbenzamides¹⁵, the Wittig-Horner condensation¹⁶ (scheme 2), the S-alkylation of thiocarbamate salts¹⁷, the Cannizzaro reaction¹⁸, and many others.



Scheme 2

A particularly illustrative case is the intriguing "sonochemical switching" described by Ando¹⁹ (Scheme 3).

Using pure aluminum oxide, the Friedel alkylation product is formed, and no influence of sonication is observed, (3h , 78%. 3h,))) 83%). With potassium cyanide on aluminum oxide, the sonochemical and the silent reactions become quite different. Under sonication, the rate of the ionic Friedel alkylation is virtually unchanged, but the substitution by the cyanide ion known to proceed in related cases through a single electron exchange pathway²⁰ is greatly accelerated, and the "substitution" product becomes predominant. Ando's sonochemical switching is then the result of the different behaviours of ionic (insensitive) and single electron (sensitive) exchanges under ultrasonic irradiation.



Scheme 3: sonochemical switching

In summary, the following points seem important to underline :

- 1- "False" sonochemical reactions of type 2 rely only on the mechanical and physical effects of sonic waves, and no "sonochemical switching" is to be expected. For most of them, they are known to proceed through ionic species which are not produced by ultrasounds.
- 2- True sonochemical reactions, either homogeneous or heterogeneous, correspond to processes in which the production of the reactive intermediate, a radical or a radical-ion, is stimulated by the irradiation with ultrasound.
- 3- When a chemical system can follow competitive ionic and radical pathways, two situations can be met. Either both of them lead to the same product(s), or different products are formed.

In the first case (convergent processes), enhancement of the radical component by sonication results in an overall rate increase. In the second case (divergent reactions) a sonochemical switching is observed, with an increased formation of the product derived from the radical pathway. As a conclusion, it was necessary to clarify the complex situation of sonochemistry and to propose an unifying theoretical approach. We think that the classification above constitutes a first step towards this goal, even if many problems remain to be studied. However, it seems that the predictive value that we had been looking for, is able to provide a better delimitation of the application domain of sonochemistry. Some illustrative examples found by following our approach are briefly discussed in the accompanying note.

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