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Scavenging of the radical species formed in the sonochemical excitation of styrenes[†]

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Abstract—The sonochemical excitation of 4-substituted styrenes in acetic acid was studied by quenching the radical species with pyrocatechol. The rate-limiting vaporization step, evidenced by the linear free energy relationship (LFER) between the excitation and the vapor pressure of the styrenes, is a characteristic of the sonochemical reactivity in a homologous series of substrates. © 2001 Elsevier Science Ltd. All rights reserved.

The discovery of the sonochemical switching has demonstrated that ultrasonic cavitation can induce a specific reactivity, independent of the rate enhancements resulting from the mechanical mixing effects.[1] A generally accepted statement is that sonication favors free radical pathways by producing such intermediates in the cavitation bubbles, in most cases via thermolytic processes. However, a general view on the sequence of events leading to this activation has not yet received an accurate formulation. If the key or initiating step of a given sonochemical reaction does occur inside the bubbles, then the required volatilization of the substrate makes cavitation-initiated reactions dependent on the vapor pressure of the reacting molecules. This deduction agrees with published examples,[2,3] even if in many cases the role of the volatility of the solvent, not of the substrate, is underlined.[2,4]

The lead tetraacetate/styrene (LTA/Sty) reaction in acetic acid is a case of sonochemical switching.[5] Sonication strongly enhances the free radical pathway giving 1-phenylpropanol acetate at the expense of the common ionic reactivity, which leads to 2-phenylethane-1,1-diol diacetate. We proposed a chain process initiated by the sonochemical formation of the styrene radical cation $[\mathrm{Sty}]^{+\bullet}$,[6] but some aspects in this mechanism are still obscure. In a continuation of this study using 4-substituted styrenes (LTA/4-X-Sty reactions), we showed that: (i) the unvolatile LTA is stable under sonication, and (ii) the usual Hammett parameters (σ, $\sigma^{\bullet}$, σ_{JJ}, etc.) do not describe the sonochemical radical reactivity, which in contrast relates satisfactorily to the vapor pressure of the styrenes.[7,8] These arguments support the central role of the formation of $[\mathrm{Sty}]^{+\bullet}$ in the bubble vapor phase.

We chose to go further with this reaction for several reasons. First, the sonication-dependent initiation step is not clearly understood. A better knowledge would be beneficial not only for the reaction itself, but also for the general understanding of sonochemical activation. Second, the LTA/Sty reactions are heterogeneous, and their analysis, technically difficult despite all the precautions, could be of limited accuracy. In addition the presence of the solid can facilitate the formation of bubbles by nucleation, and induce reactions at the surface of the crystallites. Thus, as we proposed that the $[\mathrm{Sty}]^{+\bullet}$ species form in the bubbles, we felt necessary to look for a direct proof by selective scavenging experiments in a homogeneous system omitting LTA. Pyrocatechol was chosen as the scavenger due to its ability to trap quantitatively the radicals derived from styrenes.[9]

Experiments under magnetic stirring and ultrasonic irradiation were conducted in the dark in the same thermostated cell under Ar for 3 h. The styrenes were filtered on alumina to remove the stabilizer just before use. The solutions were prepared from the purified samples or other hydrocarbons (0.5 mmol), pyrocatechol (2.2 mg, 0.02 mmol), and potassium acetate (1.27

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[†] Dedicated to Emeritus Professor Masazumi Nakagawa on the occasion of his 85th birthday.

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g, 13.0 mmol) in acetic acid (9.3 mL). An Astrason Sonicator XL2020 delivering a 20 kHz continuous wave was used at 12±1 W calorimetric intensity.[10] The sonicated and stirred reactions run at 37°C were compared by determining spectrophotometrically (MBTH method[11]) the amount of pyrocatechol decomposed and the differences between the two sets of experiments can be regarded as a sonochemical decomposition increment (Table 1).

Sonication of the solution containing styrene decomposes 13.2±0.2% of the pyrocatechol probe versus 1.9± 0.0% when stirred. The difference between the two figures reflects the amount of radical cation formed by irradiation, by the reaction sequence shown in Scheme 1, estimated by a simple calculation as 0.5% of the initial styrene. Even if seemingly small, this amount is sufficient in the reactions run with LTA, to generate the actual chain carrier species $Pb^{III}(OAc)_4^-$ in quantities sufficient for the propagation step (see Scheme 2 in Ref. 7). In contrast, *o*-xylene, of similar vapor pressure, undergoes practically no reaction. The non-aryl substituted alkene, 5-decene, of lesser ability to yield radicals, is less prone to decompose pyrocatechol even when sonicated.

Since the LTA/styrene reaction can be initiated inside the bubble, there should exist a relationship between the vapor pressure of the substrate and the amount of pyrocatechol decomposed sonochemically. For this reason, experiments were performed with several 4-substituted styrenes (4-X-Sty) under the conditions used for the reactions with LTA at 45°C, giving the results shown in Table 2.

The results shown in Table 1 were obtained at 37°C to enhance the sonochemical effects, while those in Table 2 were obtained at a slightly higher temperature (45°C) to match the conditions used in our previous investigations.[7] Even if somewhat smaller, the differences between the sonicated and stirred experiments are consistent and permit a reasonable linear free energy relationship (LFER) to be drawn between the sonochemical increment and the vapor pressures of the 4-X-Sty (Fig. 1).[14] LFER was first established with H-, Cl-, and Me-Sty (filled circles) with reliable vapor pres-

Table 1. Decomposition of pyrocatechol in the presence of various hydrocarbons

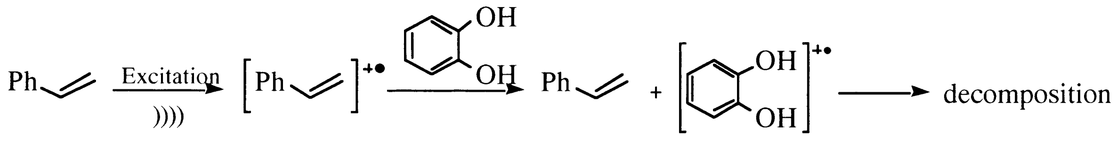
Substrate	Vapor pressure[a] (mm Hg, 37°C)	Decomposition (%)		Sonochemical increment[d]
		Ultrasound[b]	Stirring[c]	
Styrene	12.3	13.2±0.2	1.9±0.0	11.3±0.6
o-Xylene	13.0	1.4±0.6	2.2±0.6	−0.8±0.6
5-Decene	3.6	5.7±0.5	2.0±0.6	3.7±1.1
Decane	2.9	4.3±0.6	0.9±0.7	3.4±1.3

[a] Ref. 12.

[b] Average of three runs. We checked that pyrocatechol is stable under sonication.

[c] Average of two runs.

[d] Difference between pyrocatechol decomposition under ultrasound and stirring.



Scheme 1.

Table 2. Decomposition of pyrocatechol in the presence of substituted styrenes

X in 4-X-Sty	Vapor pressure[a] (mm Hg at 45°C)	Decomposition (%)[b]		Sonochemical increment
		Ultrasound	Stirring	
H	20.2	7.4±0.2	3.0±0.6	4.4±0.8
F	9.0–18.0	5.2±0.9	1.0±0.2	4.2±1.1
Me	5.8	5.8±0.4	3.4±1.1	2.4±1.5
Cl	3.0	4.0±1.0	2.5±0.1	1.5±1.1
t-Bu	0.8	5.2±0.2	3.9±0.6	1.3±0.8
Br	1.1–1.9	2.2±1.0	1.3±0.5	0.9±1.5
Blank[c]	–	1.6±0.1	1.6±0.1	0.0±0.2

[a] Ref. 13.

[b] Average of two runs.

[c] In the absence of styrene.

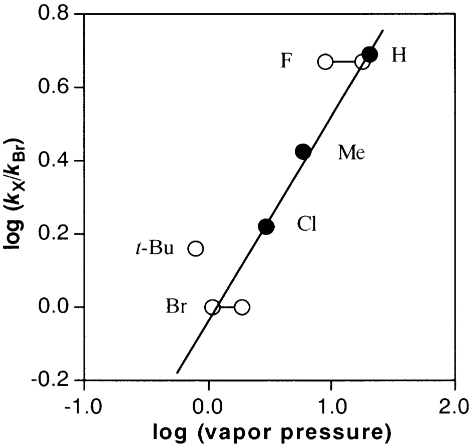


Figure 1. LFER between decomposition of pyrocatechol and 4-X-Sty vapor pressure. ●, reliable vapor pressure values (H-, Cl-, and Me-Sty); ○, less reliable values (F-, Br-, and *t*-Bu-Sty).

sure values, then F-, Br-, and *t*-Bu-Sty (open circles) with less reliable values were added.

Basically, the intracavity reactions must depend on the number of molecules vaporized and their intrinsic ability to undergo thermolysis, ionization, coupling with radicals, etc. The fact that we observe this good LFER confirms that vaporization is determining for the subsequent sonochemical reactions, including (and especially in) the cases where a switching takes place. It even suggests that a 'vapor pressure substituent constant' could be used to describe other gas phase reactions of a homologous series of aromatic compounds. This must be one of the important characteristics of sonochemistry. Under the extreme conditions of cavitation, the intrinsic reactivity of each species appears of lesser importance, which nevertheless will be assessed in a future work.

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8. Here, the vapor pressure is taken into account in preference to the evaporation rate (Ref. 4a), or the heat of vaporization. This simplification is justified at this stage of the work, by the difficulty to determine the exact behavior of a non-polar solute diluted in the polar, strongly self-associated solvent AcOH.
9. *t*-Butylcatechol, used as a stabilizer at 10–50 ppm concentrations in commercial styrenes, depresses the radical pathway in the styrene-LTA reaction. See: Norman, R. O. C.; Thomas, C. B. *J. Chem. Soc. (B)* **1967**, 771–779.
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14. The free energy term for the decomposition of pyrocatechol was approximated by the following equation, as it can be regarded as a pseudo-first order reaction at small conversions:

$$\log(k_X/k_{Br}) = \log(\text{yield}_X/\text{yield}_{Br})$$