

Sonochemical Reactions of Lead Tetraacetate with 4-Substituted Styrenes

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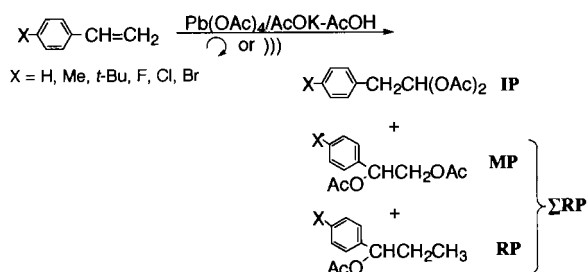
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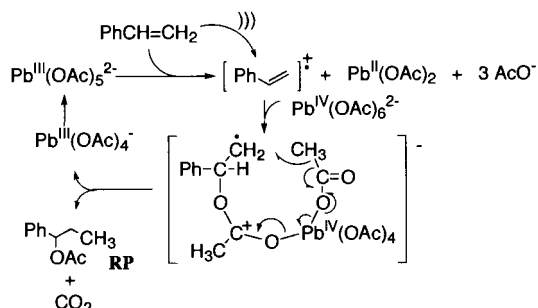
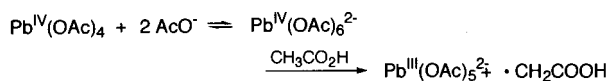
A good linear free energy relationship was observed between the radical reactivity of the sonochemical reactions of 4-substituted styrenes with lead tetraacetate and the vapor pressure of the styrenes, indicating a probable control of the process by an intra-bubble activation.

The reaction of lead tetraacetate (LTA) with styrene can be considered as a typical case of sonochemical switching.¹ Under conventional conditions, an ionic pathway predominates which yields compound **IP** (Scheme 1).²



Scheme 1.

Ultrasonic irradiation leads to a dramatic reactivity change, even at 45 °C, similar to or even greater than that observed in refluxing acetic acid (116 °C), and the products resulting from a radical process (**RP** and **MP**) become the major ones.³ Recently⁴ we proposed a mechanism which agrees with our experimental results and explains the role of acetate ions (Scheme 2).⁵ According to this Scheme, the sonochemical excitation can occur either at the radical decomposition of hexa-acetato-lead(IV) ion to the key Pb(III) species or at the excitation of styrene to its radical cation. The former process should take place at the gas-liquid interface because of the lack of the vapor pressure of the Pb(IV) species and the latter in the gas phase of the cavity under thermally extreme conditions.⁶



Scheme 2.

A classical method used for the study of reaction mechanisms of aromatic substrates being the linear free energy relationship (LFER) observed by the introduction of substituents on the ring, we investigated the behavior of a few 4-substituted styrenes with the hope to discriminate the above two possibilities.

The experiments were conducted in the dark under argon. Stirred reactions⁷ were run at 45 °C in a thermostated vessel, with the required styrene (2.5 mmol), LTA (3 mmol) and AcOK (15 mmol) suspended in acetic acid (10 mL). The sonochemical experiments were performed at 45 °C in a thermostated cell, with an Astrason Sonicator XL 2020 delivering a 30-W (calorimetric⁸) 20-kHz continuous wave. In both series of experiments, the reaction was quenched after 3 h by addition of aq NH₄Cl, and the organic compounds were extracted with ether. The ethereal layer was washed (aq NaHCO₃, then water) and the mixture analyzed by VPC with dodecane as an internal standard. The results are shown in the Table 1.

Table 1. Reaction and vapor pressure of substituted styrenes

X	Vapor Pressure at 45°C/mmHg	Conditions ^a	Yield/%			
			RP	IP	MP	Recovered
H	20.2	M	0.0	24.0	0.0	48.5
		U	70.0	8.0	8.0	6.0
F	9.0 - 18.0	M	0.0	23.2	0.0	42.8
		U	35.9	13.9	7.9	13.7
Me	5.8	M	2.1	66.0	4.2	7.6
		U	22.0	40.0	27.0	3.0
Cl	3.0	M	0.0	7.2	0.0	74.5
		U	28.9	3.2	3.2	32.0
<i>t</i> -Bu	0.8	M	0.0	59.0	0.0	12.6
		U	10.3	29.9	14.6	29.6
Br	1.1 - 1.9	M	0.0	4.9	0.6	82.4
		U	13.8	2.5	2.9	53.6

^aM : Magnetic stirring, U : Ultrasound.

Because of the heterogeneous nature of the mixture, kinetic studies proved to be technically difficult; only the final percentages of the products were obtained with a satisfactory accuracy. Nevertheless attempts to correlate the free energy differences to the properties of the substituted styrenes were undertaken. The free energy term was approximated by the following equation.⁹

$$\log(k_x/k_{Br}) = \log \frac{\ln(100 / (100 - \text{yield}_x))}{\ln(100 / (100 - \text{yield}_{Br}))} \quad (\text{eq 1})$$

When the ionic reactivity under the conventional conditions is considered, good LFER was observed with the Hammett σ^+ (Figure 1, Curve 1, $\rho^+ = -2.81$, $r = 0.979$), in accord with the admitted mechanism of an initial electrophilic

attack by the triacetato-lead cation on the double bond. As expected, sonication does not change the aspect of the curve at all (Figure 1, Curve 2, $\rho^+ = -2.81$, $r = 0.992$).

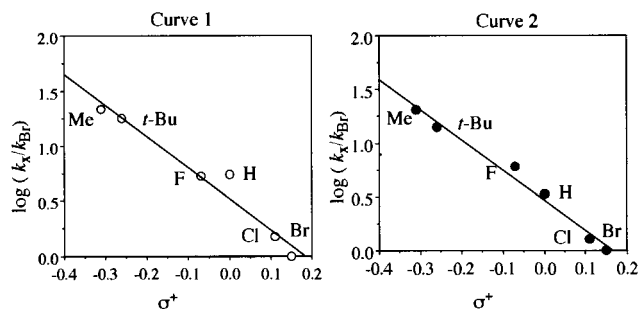


Figure 1. LFER of IP vs σ^+ . Curve 1 for stirred experiments, curve 2 for sonochemical ones.

Practically no **RP** is formed under stirring. In the sonicated reactions, all the attempted LFER between the radical reactivity and various substituent constants including those representing the radical reactivity such as σ_{JJ} fail.¹⁰ We have established previously that the decomposition of LTA in the absence of styrene is not greatly influenced by sonication,^{3d} but this decomposition can generate a lead(III) species,¹¹ which can initiate a chain process. By considering the characteristics of sonochemistry and the mechanism proposed, it can be deduced that (i) cavitation is most important to induce the radical reactivity and (ii) the only compound able to penetrate into the cavitation bubble is the styrene partner. Then, some relationship between the radical reactivity and the volatility of styrenes should exist. The vapor pressures of substituted styrenes at 45 °C were estimated by the use of the Clapeyron–Clausius equation and listed in Table 1. Enough data are available for H-, Cl- and Me-substituted styrenes to establish the slopes and intercepts of the equation.¹² For F-, Br- and *t*-Bu-styrenes, for which only scattered data of the boiling points at reduced pressures are available, estimation was carried out by taking advantage of the similarity to the above styrenes.

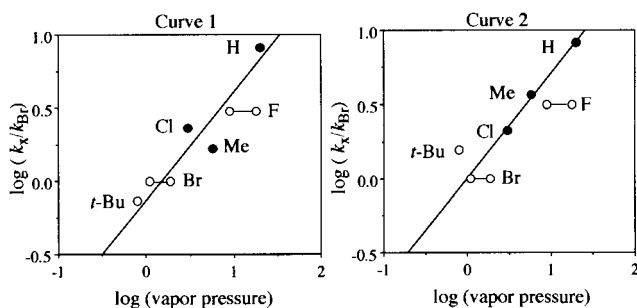


Figure 2. LFER for **RP**(curve 1) and Σ **RP**(curve 2) vs vapor pressure.

The good LFER between the vapor pressure term and the radical reactivity term estimated from **RP** yields and Σ **RP** yields is apparent in Figure 2, Curves 1 and 2, in spite of the rough estimation and the inaccuracy of the reactions run under

sonication. The conclusion should be that in this reaction, and probably in other sonochemical systems, the ability of a substrate to vaporize into the gas phase of the cavitation bubble is a critical step. In addition, our mechanism proposed for the reaction of LTA with styrene is further confirmed; the sonochemical effect is attributed to the excitation of styrene to its radical cation and not the sonication enhanced radical decomposition of hexaacetato-lead(IV) ion.

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