Sonochemical Switching from Ionic to Radical Pathways in the Reactions of Styrene and *trans*-ß-Methylstyrene with Lead Tetraacetate

Takashi Ando,*^a Patrick Bauchat,^a André Foucaud,^b Mitsue Fujita,^a Takahide Kimura,^a and Hajime Sohmiya^a

^a Department of Chemistry, Shiga University of Medical Science, Otsu, Shiga 520-21, Japan

^b Groupe de Physicochimic Structurale associé au C.N.R.S., Université de Rennes, Campus de Beaulieu, 35042 Rennes, France

Key Words: sonochemistry; sonochemical switching; lead tetraacetate; styrene; trans-\u00b3-methylstyrene

Abstract: The reactions of styrene and trans- β -methylstyrene with lead tetraacetate in acetic acid are greatly influenced by ultrasonic irradiation to give products resulting mostly from radical chain pathways, whereas mechanical agitation gives products only from ionic processes.

A large number of papers describing the successful use of ultrasonic irradiation in organic synthesis have been published in the last few years. However, most of them are those of simple acceleration of solid-liquid heterogeneous reactions of metals which could be attributed at least partly to the cleaning effect of the metal surface. Examples of sonochemical switching, i.e., specific acceleration of a reaction pathway under sonication different from that under mechanical stirring, have been reported in only limited cases.¹⁻⁴ Here we report clearcut examples in which ultrasonic irradiation not only accelerates the reaction but also dramatically changes the reaction pathway from ionic to radical.

$$PhCH=CH_{2} \xrightarrow{Pb(OAc)_{4}/AcOH}$$

$$Ph \xrightarrow{Ph} \xrightarrow{Ph} \xrightarrow{Ph} \xrightarrow{Ph} \xrightarrow{PhCH_{2}OAc} + PhCH_{2}CH(OAc)_{2} \quad (1)$$

$$AcO \xrightarrow{(I)} \quad (II) \quad (III) \quad (III)$$

Styrene reacts with lead tetraacetate in acetic acid to give a variety of products depending on the reaction conditions [eqn. (1)]. Mechanisms of the reaction have been studied well and are interpreted by the competing

ionic and radical pathways.^{5,6} Compound I results from a radical chain reaction and III from an ionic process, whereas compound II is regarded to be formed by the two concurrent reactions.

A mixture of styrene (2.4 mmol) and lead tetraacetate (3.0 mmol) in acetic acid (5.5 ml) was stirred with a magnetic stirrer or subjected to ultrasonic irradiation at a given temperature in the dark under nitrogen. An Astrason SONICATORTM W-385 (Heat Systems-Ultrasonics, 20 kHz) was used at the power of 190 W for sonication in the following two manners: (A) a sonochemical reactor similar to that described by Suslick⁷ or Luche⁸ with a sonic horn directly immersed into the reaction solution and a thermostated jacket or (B) a cup-horn device which is regarded as a small cleaning bath.

After a given reaction period the mixture was poured into water and extracted with ether. The products were analyzed by GLC with dodecane as an internal standard. As reported in the literature,⁵ three major products (I-III) were obtained and identified by comparison with authentic samples. Small amounts of the two hydroxy acetates (IV and V), phenylacetaldehyde (VI) and benzaldehyde (VII) were also detected in addition to the starting material, styrene. Traces of other peaks appeared in the chromatogram but were not identified. The results are summarized in Table 1, in which only the yields of I-III are shown.



Table 1. The Effect of Ultrasound on the Reaction of Styrene with Lead Tetraacetate.

				Product yield/%		
Entry	Conditionsa	Temp/°C ^b	Time/h	Ι	II	ш
1	М	12	1	0	0	0
2	М	50	1	0	0	5.2
3	М	50	15	0	0	33.1
4	Μ	80	1	11.2	0	21.7
5	М	100	1	36.0	7.5	11.0
6)))A	12	1	14.6	8.4	3.0
7)))A	50	1	38.7	12,4	2.7
8)))A	62	1	46.0	8.3	3.5
9)))A ^c	50	1	1.0	0	8.5
10)))Ad	50	1	0	0	4.5
11)))B	12	1	0	0	0
12)))B	50	1	0.3	0	25.0
13	_)))Be	50	1	15.5	9.0	17.8

^a M, Mechanical agitation using a magnetic stirrer;)))A, ultrasonic irradiation using a sonochemical reactor at 190 W;)))B, ultrasonic irradiation using a cup-horn at 190 W. ^b Temperature was measured inside the reaction vessel just after the reaction. See the text, ^c p-Benzoquinone (0.56 mmol) was added. ^d 4-t-Butylcathecol (0.6 mmol) was added. ^e At 380 W.

Reproducibility of the results was good even under ultrasonic irradiation when the reaction conditions including the geometry of the sonochemical reactor were kept constant.

With mechanical agitation only III, the product of the ionic pathway, was obtained at 50 °C or lower reaction temperatures (entries 1-3). At higher temperatures the radical pathway intervened (entry 4) and became predominant at 100 °C (entry 5). Under direct sonication in an ultrasonic reactor, the reaction proceeded even at 12 °C (entry 6), the radical pathway being predominant. The radical pathway became overwhelming at higher temperatures (entries 7 and 8). When a radical scavenger such as p-benzoquinone or 4-t-butylcatechol was added, the radical pathway was almost inhibited and a small amount of III was obtained (entries 9 and 10). Interestingly, indirect ultrasonic irradiation in a cup-horn at the same power of 190 W only accelerated the ionic process to give III and no sonochemical switching was observed (entry 12). The radical product I was obtained when the power was doubled to 380 W (entry 13).

trans-β-Methylstyrene is also known to react with lead tetraacetate to give the products resulting from radical (VIII and IX) and ionic (X and XI) processes [eqn. (2)].^{9,10} We found that sonochemical switching took place in this reaction in a similar manner to that shown for styrene. Table 2 shows that direct ultrasonic irradiation switched the main reaction pathway from ionic to radical (entry 2 vs entry 1). In this case, indirect ultrasonic irradiation in a cup-horn at 380 W gave qualitatively similar results as those under the direct irradiation.



Table 2. The Effect of Ultrasound on the Reaction of *trans*-B-Methylstyrene with Lead Tetraacetate.^a

				Product yield/%			
Entry	Conditionsb	Temp/°C ^c	Time/h	VIII	IX	x	XI
1 ^d	М	50	24	0	0	12.5	24.3
2)))A	50	1	29.2	34.6	3.9	0.5
3)))B	50	1	16.2	14.8	3.2	0

^a Starting materials: *trans*-ß-methylstyrene, 1.4mmol; lead tetraacetate, 1.4mmol; AcOH, 5.5ml; AcOK, 15mmol.^bM, Mechanical agitation using a magnetic stirrer;)))A, ultrasonic irradiation using a sonochemical reactor at 190 W;)))B, ultrasonic irradiation using a cup-horn at 380 W. ^c Temperature was measured inside the reaction vessel just after the reaction. See the text. ^dBenzaldehyde was obtained in the yield of 17%.

For the experiments with mechanical agitation, it is apparent that a higher temperature favors the radical pathway. This observation is in agreement with that reported by Norman and Thomas.⁵ For sonication reactions, the temperature was determined before and after the reaction, the former being lower than the latter by about 5 °C. The temperatures cited in Tables 1 and 2 for sonication reactions were those just after the reactions. Thus, they were the maximum values during the course of the reaction. Therefore, the observed sonochemical switching from the ionic to radical pathway cannot be attributed to a gross temperature effect.

According to the hot spot theory of ultrasonic cavitation, the local effective temperature rises up to thousands of degrees during the effective lifetime of less than several μ s.¹¹ Although it is not conclusive at present, our results can be explained by the evolution of these hot spots, in which the thermal environment is different from the external heating. The difference between the results obtained under sonication at a lower temperature (entry 7 in Table 1) and those obtained under mechanical agitation at a higher temperature (entry 5 in Table 1) can be attributed to this different thermal environment.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. We are also grateful to Japan Society for the Promotion of Science for a Fellowship to P.B.

References and Notes

- 1. Ando, T.; Sumi, S.; Kawate, T.; Ichihara, J.; Hanafusa, T. J. Chem. Soc., Chem. Commun., 1984, 439.
- (a) Suslick, K.S.; Schubert, P.F.; Goodale, J. W. J. Am. Chem. Soc., 1981, 103, 7342. (b) Suslick, K. S.; Goodale, J.W.; Schubert, P.F.; Wang, H.H. *ibid.*, 1983, 105, 5781.
- 3. Einhorn, J.; Einhorn, C.; Luche, J.-L. Tetrahedron Lett., 1988, 29, 2183.
- 4. Einhorn, C.; Einhorn, J.; Dickens, M.J.; Luche, J.L. Tetrahedron Lett., 1990, 31, 4129.
- 5. Norman, R.O.C.; Thomas, C.B. J. Chem. Soc. (B), 1967, 772.
- 6 Norman, J.A.; Thomas, C.B.; Burrow, M.J. J. Chem. Soc., Perkin Trans. 1, 1985, 1087.
- 7. Suslick, K.S.; Johnson, R.E. J. Am. Chem. Soc., 1984, 106, 6856.
- 8. de Souza-Barboza, J.C.; Pétrier, C.; Luche, J.-L. J. Org. Chem., 1988, 53, 1212.
- 9. Norman, R.O.C.; Thomas, C.B. J. Chem. Soc. (B), 1968, 994.
- 10. Heiba, E.I.; Dessau, R.M.; Koehl, W.J., Jr. J. Am. Chem., Soc., 1968, 90, 2706.
- 11. Suslick, K.S.; Hammerton, D.A.; Cline, R.E., Jr. J. Am. Chem. Soc., 1986, 108, 5641

(Received in Japan 22 August 1991)