The Site of the Sonochemically-Initiated Radical Reaction of Lead Tetraacetate with *β*-Methylstyrene

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The effective temperature of the radical propagation step of the ultrasonically accelerated reaction of lead tetraacetate with β-methylstyrene was thermodynamically determined as close to the ambient temperature of the bulk liquid.

Characteristic sonochemical reactions in homogenous solutions originate from excited-state species created in acoustic cavitation: formation and collapse of microbubbles under the irradiation of power ultrasound. According to the 'hot spot' theory, cavitation causes extremely high temperatures and high pressures. Several experimental studies indicated that the effective temperature reaches as high as 5000 K.[1] Consistent with this theory, irradiation of ultrasound often switches the course of a reaction from ionic to radical.[2]

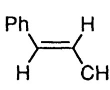
Contrary to the radical initiation step which takes place at extremely high temperatures in the cavitation process, the radical propagation step is rather arbitrarily believed to proceed at ambient temperatures without any definite experimental study.[3] In the present study, we thermodynamically determined the effective temperature of the radical propagation step in the reaction which is selectively accelerated under ultrasonic irradiation.

Lead tetraacetate in acetic acid reacts with *trans*-β-methylstyrene **1** through the competing radical and ionic mechanisms; a higher temperature favors the radical pathway.[4,5] We recently found that irradiation of ultrasound not only accelerates the reaction but also greatly affects the course of the reaction.[2] It turned out to be a clear-cut example of the sonochemical switching from the ionic pathway to the radical one even at lower temperatures.

Heiba observed that the relative yield of the two main radical reaction products [**3**]/[**2**] varies with changes in the [acetic acid]/[**1**] ratio, the reciprocal of the concentration of **1** in the solvent acetic acid.[4] This linear relationship is consistent with the competition reaction of the methyl radical either with **1** or with acetic acid in the free radical chain mechanism (Scheme I). From the variation in the slope of the relative reactivity at various temperatures, they calculated that the difference in the activation energies was 1.7 kcal/mol favoring **3** at a higher temperature.

If this approach can be followed in the reverse direction, we must be able to determine the effective temperature of the actual reaction site of the particular radical propagation reaction. In other words, the relative reactivity of **3** to **2** must indicate the effective temperature of the environment surrounding the methyl radical. Under similar reaction conditions to those of Heiba with magnetic stirring, the reaction was carried out at 60, 80, and 130 °C (Figure 1).[6] Although the linearity was not so excellent as that reported by Heiba[4], the difference in the activation energy calculated from these plots, 3.0 kcal/mol, was in fair agreement with the literature value. The ratio of the pre-exponential factors was unity. Then, the reaction was carried out under ultrasonic irradiation at 60.0±2.8 °C. The temperature determined just after the reaction with a thermocouple inherently had larger uncertainty because of the exothermicity under ultrasonic irradiation. From the plots shown in Figure 1, the actual reaction temperature was determined as 74 °C.[7]

An alternative approach is possible based on the assumption that only the increments in the yields correspond to the products obtained under the influence of ultrasound. In other words, the observed yields are the sums of those of the usual thermal reaction and the sonochemical reaction. This approach was carried out at one particular concentration of **1** in acetic acid to give the temperature of 98 °C.[8]



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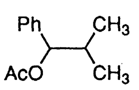

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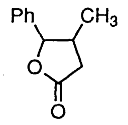

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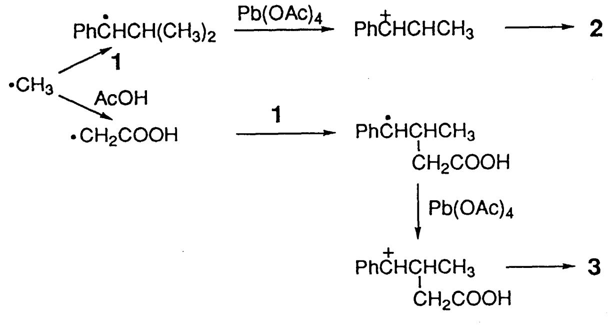
Scheme I



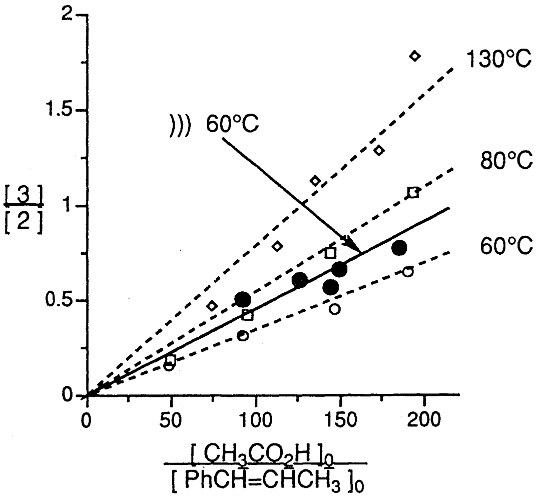


Figure 1. Relative reactivity of the methyl radical to acetic acid vs. **1** at various temperatures under stirring and ultrasonic irradiation.

Insufficient accuracy involved in the present study, especially the difficulty in controlling the temperature under ultrasonic irradiation and the poor linearity of the plots shown in Figure 1, restricts the detailed discussion concerning the characteristics of the reaction site. Nevertheless, either approach shown above clearly indicate that the reaction site of the radical propagation step of the sonochemically-initiated chain reaction is not in the collapsing cavity nor in the boundary liquid shell of a very high temperature but mostly in the bulk liquid phase of an ambient temperature. The present study proves to be the first experimental observation of the nature of the sonochemically-initiated radical chain reaction site.[9]

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References and Notes

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6 Temperature was kept within ±0.3 °C. The yields of **2** and **3** were determined after 8 h. Each point was the average of duplicate runs.

7 The yields were determined after 3 h. Each point was the average of duplicate runs.

8 The reaction was carried out twice under stirring and three times under ultrasonic irradiation with [acetic acid]/[**1**] = 124 at 60 °C for 2 h. The yields (%) of **2** and **3** were 10.9± 0.9 and 3.7± 0.2, respectively under stirring, while 30.1±3.3 and 17.6±4.7, respectively under ultrasonic irradiation. Only the increments were regarded to be obtained under the influence of ultrasound.

9 During the process of publication of this work, we learned that Prof. J. Reisse and his group of Université Libre de Bruxelles independently obtained similar results. We are grateful to Prof. Reisse for informing us their results before publication.