Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate with Ultrasonic Irradiation. The Possibility of the Formation of Supercritical Water

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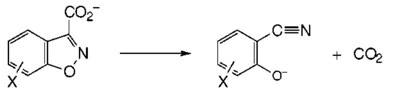
In 1995, Hoffmann and co-workers proposed the possible formation of transient supercritical water in the hydrolysis of *p*-nitrophenyl acetate with ultrasonic irradiation.[1] Their proposal depends on the observations of rate acceleration of 2 orders of magnitude, the rate independence of pH and ionic strength, and characteristic activation parameters. As it is an established idea that acoustic cavitation produces high temperatures and pressures exceeding the critical values of water (647 K and 221 bar), there is a distinct possibility of the formation of supercritical water, although its lifetime and volume might be questionable. Considering the rapidly increasing importance of supercritical water as a reaction medium of chemical transformations, we tried to detect the possible formation of supercritical water with a different approach.

The rates of decarboxylation of benzisoxazole-3-carboxylates (eq 1) are strongly dependent on the reaction medium. In the detailed solvent-effect studies, Kemp and co-workers showed that the first-order rate varies up to 8 orders of magnitude on going from reaction in water to reaction in dipolar aprotic solvents such as *N*,*N*-dimethylformamide.[2] This has been explained by (1) stabilization of the starting carboxylates by hydrogen bonding in protic media and (2) stabilization of the charge-delocalized transition state through dispersion interactions with polarizable media. The reaction has been widely used to investigate the microenvironment of the medium.[3] As supercritical water has solvent properties completely different from those of water under normal conditions, it is reasonable to expect that the decarboxyation rate of benzisoxazole-3-carboxylates must vary considerably with ultrasonic irradiation if a supercritical state is formed.



(1)

1 (X = 6-NO_2)

Table 1. Rate Constants for the Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate

	temp (°C)[a]	k (s^{-1})
	Method A	
ultrasound	30.4	8.32×10^{-6}
	31.4	8.29×10^{-6}
	40.0	3.10×10^{-5}
	40.4	8.23×10^{-5}
	48.4	1.26×10^{-4}
	49.7	1.35×10^{-4}
stirring	30.4	6.17×10^{-6}
	40.5	3.58×10^{-5}
	50.7	1.89×10^{-4}
	Method B	
ultrasound	30.0	6.56×10^{-6}
	30.2	6.35×10^{-6}
	30.7	6.95×10^{-6}
	37.9	2.26×10^{-5}
	38.5	2.04×10^{-5}
	38.9	2.33×10^{-5}
	48.5	0.90×10^{-4}
	48.8	1.14×10^{-4}
	49.3	0.97×10^{-4}
stirring[b]	30.4	$(6.80 \pm 0.13) \times 10^{-6}$
	40.5	$(3.71 \pm 0.12) \times 10^{-5}$
	50.7	$(1.65 \pm 0.05) \times 10^{-4}$

[a] For stirring, ±0.1 °C; for ultrasound, see the text. [b] Average of two runs.

Decarboxylation was carried out for 6-nitrobenzisoxazole-3-carboxylic acid (**1**) as a substrate in phosphate-buffered solutions at pH 7.0 under argon. Reaction solutions were prepared with two methods: (A) dilution of a concentrated ethanol solution of **1** with a buffered solution or (B) direct dissolution into a buffered solution and filtration. The reaction was followed spectrophotometrically at 395 nm. Isosbestic points were observed in all the kinetic experiments with both ultrasonic irradiation and magnetic stirring. A horn type sonicator, Astrason Sonicator XL 2020 (Heat System-Ultrasonics, 20 kHz), was used for ultrasonic irradiation at an acoustic intensity of 12 ± 1 W.[4] Excellent linear plots ($r > 0.999$) were obtained for more than two half-lives except for the kinetic runs at low temperatures with ultrasonic irradiation, in which precipitation of metal powder hindered the accuracy ($r > 0.997$ for one half-life).

The results are summarized in Table 1. It is evident that the effect of ultrasonic irradiation is not large. The ratios of the calculated rate constants at 40 °C with ultrasonic irradiation versus magnetic stirring are 1.01 for method A and 0.87 for method B. Two methods of preparation of reaction solutions, A and B, were adopted to avoid the possible disturbance of the formation of supercritical water with an alcohol cosolvent,[1] but this choice does not have much effect. Activation parameters are calculated as shown in Table 2. All the kinetic data are similar to those reported by Kemp et al.[2]

Somewhat slower rates with ultrasonic irradiation, especially apparent for the method B series, can be attributed to the temperature inhomogeneity inside the

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Table 2. Activation Parameters for the Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate[a]

	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
	Method A	
ultrasound	120 (4)	53 (14)
stirring	135 (1)	99 (1)
	Method B	
ultrasound	116 (3)	38 (10)
stirring	125 (3)	70 (9)

[a] Estimated errors are shown in parentheses.

reaction vessel. Evolution of heat inside the vessel near the horn and cooling outside the vessel cause the temperature deviation of 1.3 °C at the maximum at the reaction temperature of 50 °C. Throughout the series of kinetic experiments, the temperature was measured at the same position showing a rather high temperature.

It is also worth noting that differences in the activation parameters, smaller $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with ultrasound, are apparently greater than estimated errors (Table 2). However, the temperature inhomogeneity described above makes the detailed discussion difficult.

It is not easy to estimate the properties of such transient supercritical water if it is formed. It is generally considered that supercritical water behaves like organic solvents with low densities and low dielectric constants such as acetone.[5] The rate constant of decarboxylation of **1** in acetone was reported to be 3 × 10^6 times faster than that in water.[2] Although there is a possibility of a rate decrease caused by the higher ion product of supercritical water, it must not be so large as the decarboxylation rate is almost constant for the range of pH above 3.[2] Thus, the formation of supercritical water with ultrasonic irradiation could not be proved in this study. However, the absence of a sonochemical effect in the decarboxylation of **1** does not necessarily mean that supercritical water is not formed in the water with ultrasonic irradiation, as the present reaction may not be an adequate probe for the formation of supercritical water.

Aqueous sonochemistry is generally attributed to the initial decomposition of water for producing hydroxyl radical and hydrogen or pyrolysis of substrates in the process of cavitation. Another possibility of the mechanism, the formation of supercritical water, must be pursued further from a different point of view considering the importance of aqueous sonochemistry in the industrial application.

Experimental Section

6-Nitrobenzisoxazole-3-carboxylic acid (**1**) was prepared according to the literature,[3a,e,6] mp 188.0−189.5 °C (lit.[6] mp 189−190 °C).

Decarboxylation of 1 was carried out in phosphate-buffered solutions at pH 7.0 under argon. Reaction solutions were prepared with two methods. (A) **1** (18.3 mg) was dissolved in ethanol (0.5 mL), and 0.25 mL of the ethanol solution was added into 9.2 mL of the buffered solution. (B) **1** (10−12 mg) was directly dissolved in a buffered solution (12 mL), and 9.4 mL of the solution was used after filtration. The reaction was followed spectrophotometrically at 395 nm by using a Shimadzu UV−Vis recording spectrophotometer (UV-260).

Ultrasonic irradiation was administered by using an Astrason Sonicator XL2020 (Heat System-Ultrasonics, 20 kHz). The reactor was a cylindrical and jacketed glass vessel fitted with an immersible 0.5 in. horn. The temperature inside the reaction vessel was monitored with a thermocouple. In all the sonochemical experiments, the electric power was 165 W and the acoustic intensity was 12 ± 1 W.[4] The same glass vessel was used for reactions with magnetic stirring.

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