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Difference between Sonolysis and Photolysis of Bromotrichloromethane in the Presence and Absence of 1-Alkene

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Introduction

Reactions characteristic of ultrasonic irradiation have been named sonochemistry and have become topical in recent years. It has already been established that sonochemical reactions originate by cavitation, i.e., the formation and collapse of micro bubbles, which generate the so-called hot spot.[1] In the hot spot the local temperature rises up to thousands of degrees and the local pressure rises up to hundreds of atmospheres, which produces excited species and promotes reactions while the bulk liquid is kept at ambient temperature. Through this activation process, sonication induces a specific chemical reactivity, and radical reactions are generally regarded as preferential processes.[2] The detailed mechanism of the sonochemical excitation, however, is still unclear.

To elucidate the excitation mechanism in sonochemistry, we performed a comparison between the sonolysis and photolysis of bromotrichloromethane ($BrCCl_3$) in the presence and absence of 1-alkenes. It is interesting to study the difference in sonochemical and photochemical processes of the same reaction, which must reflect the difference in the activation mechanisms. Irradiation of either ultrasound[3] or UV light[4] causes fragmentation of $BrCCl_3$ to a bromine atom and a trichloromethyl radical. The radicals produced may recombine to form the starting $BrCCl_3$ or dimerize to bromine (Br_2) and hexachloroethane (Cl_3CCCl_3). In the presence of 1-alkene, the radicals attack 1-alkene to give an adduct ($RCHBrCH_2CCl_3$) by the following chain reaction process, together with a bromine adduct ($RCHBrCH_2Br$) (Scheme 1). This reaction does not proceed without ultrasound or light, in the absence of an initiator such as a peroxide.[5]

Scheme 1

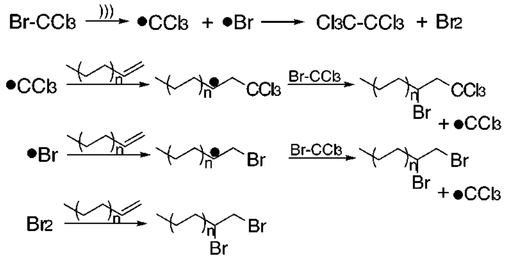

Table 1. Comparison between Sonochemical and Photochemical Reactions of Bromotrichloromethane with or without 1-Alkene

	conditions[a]			yields (mmol)		
run	irradn	alkene	DPPH (mmol)	Cl_3CCCl_3	Br_2 adduct	$BrCCl_3$ adduct
1	)))			0.030		
2	)))		0.2	0.025		
3	)))		0.4	0.029		
4	$h\nu$			0.000		
5	)))	1-octene		0.085	0.092	0.204
6	)))	1-octene	0.2	0.023	0.049	0.002
7	$h\nu$	1-octene		0.082	0.061	2.093
8	)))	1-octene/ 1-hexene		0.053	0.033/ 0.031	0.208/ 0.206

[a] 1-Alkenes (4 mmol) in $BrCCl_3$ (total 10 mL). Ar, 30 min, 10 °C.

Experimental Section

The 20 kHz ultrasonic irradiation was performed using a Heat System immersion horn (model XL 2020) equipped with a titanium probe. The acoustic intensity introduced into the reaction solution was about 20 W as measured by calorimetry.[6] Bulk temperature during sonication was maintained at 10 °C by circulating water. The photoreaction was performed by using a mercury lamp (Toshiba H400-P) in a Pyrex glass vessel, jacketed with circulating water. The light was not filtered. Reaction temperature during the irradiation of light was maintained at 10 °C.

$BrCCl_3$ was purchased from Tokyo Kasei (Japan) and 1-octene, 1-hexene, and 2,2-diphenyl-1-picrylhydrazyl (DPPH) from Wako Pure Chemicals (Japan). They were used without further purification.

1-Alkene (4 mmol) in $BrCCl_3$ (total volume of a reaction mixture, 10 mL) was irradiated for 30 min under an Ar atmosphere. Then the reaction mixture was analyzed by gas chromatography.

Results and Discussion

The results are summarized in Table 1. In the absence of 1-alkene, the dimer Cl_3CCCl_3 was the only reaction product other than Br_2 (Table 1, run 1). Even when a nonvolatile radical scavenger, DPPH, was added to the reaction mixture at a concentration of either 20 or 40 mM, the yield of the Cl_3CCCl_3 dimer did not decrease (Table 1, runs 2 and 3). We suggest that the fragmentation of $BrCCl_3$ and the dimerization of trichloromethyl radical occurs in the gas phase of the cavity and that the radicals cannot be trapped efficiently with a scavenger of low vapor pressure.

In the presence of 1-octene, the expected adducts ($C_6H_{13}CHBrCH_2CCl_3$ and $C_6H_{13}CHBrCH_2Br$) were obtained by the irradiation of either ultrasound or light (Table 1, runs 5 and 7). When DPPH was added under sonication, the yields of the adduct ($C_6H_{13}CHBrCH_2CCl_3$)

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decreased sharply (Table 1, run 6). We believe this shows that the radical chain reactions, proceeding in the bulk liquid, can be efficiently quenched with DPPH. A competitive reaction of 1-octene and 1-hexene proves that these alkenes have similar reactivity and give equal amounts of the respective adducts under ultrasonic irradiation (Table 1, run 8). The calculated vapor pressures of 1-octene, 1-hexene, and bromotrichloromethane are 7.3, 95.3, and 19.0 mmHg at 10 °C, respectively.[7] If the addition of trichloromethyl radical to alkenes takes place mainly in the gas phase, the difference in the vapor pressure of 1-octene and 1-hexene should give the adducts in different yields. Thus, these results indicate that the radical chain propagation reaction occurs in the bulk liquid phase. Presumably, some of the radicals formed in the gas phase, in the cavitation process, dimerize to give Cl_3CCCl_3 in the gas phase, while the surviving radicals migrate into the surrounding liquid phase to initiate the radical chain propagation.

In contrast to the sonochemical reaction, the photochemical reaction in the absence of 1-alkene did not give the dimer Cl_3CCCl_3 (Table 1, run 4). But when 1-octene was added to the reaction solution, the dimer Cl_3CCCl_3 was detected in addition to the adducts. The fact that the presence of alkene afforded products including Cl_3CCCl_3, implies that even in the absence of alkene, $BrCCl_3$ does produce CCl_3 radical. Thus, in the photochemical reaction we can conclude that the radical is produced in a dispersed state and its local concentration is low. The dimer is produced only in the chain propagation step.

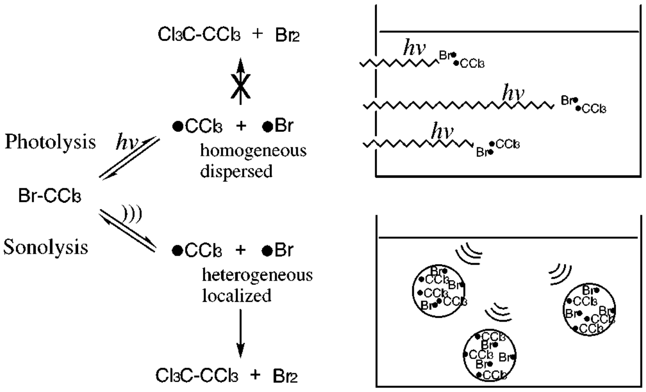

Figure 1. Schematic illustration of the difference between sonolysis and photolysis of $BrCCl_3$.

The present results clearly show that UV light generates radicals in a homogeneous and dispersed state, while cavitation generates them in a heterogeneous and localized state as illustrated in Figure 1. It can thus be concluded that photolysis and sonolysis are different in a physical sense, even though the reaction itself can be written in the same chemical equations.

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