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Homogeneous Sonochemistry: A Study of the Induced Isomerization of 1,2-Dichloroethene under Ultrasonic Irradiation

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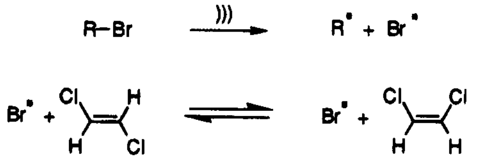
Introduction

The increasing interest in sonochemistry necessitates quantitative studies in order to obtain a better understanding of what happens at molecular level, in a cavitating liquid which has been submitted to high intensity ultrasonic irradiation. We performed a quantitative study of the isomerization of 1,2-dichloroethene (**1**) induced by the reversible addition of a bromine radical. The sonochemical step of this reaction is the homolytic cleavage of a bromoalkane (R−Br) leading to the formation of a bromine atom and an alkyl radical. The following reversible addition of the bromine atom to the carbon−carbon double bond allows the ethylenic compound to isomerize by free rotation around the single bond of the reaction intermediate.



Experimental Section

The 20 kHz ultrasonic irradiation was performed by using an Undatim Ultrasonics S.A. immersion horn system equipped with a titanium probe. The acoustic intensity, constant during the experiment, was adjusted in order to be just above the transient cavitation threshold. Bulk temperature during sonication was maintained at 10 ± 1 °C.

Solvent and reactants of the highest purity grade were purchased from Aldrich Chemical Co. and were used without further purification.

Irradiated CCl_4 solutions were 0.21 M in 1,2-dichloroethene and 0.15 M in bromoalkane. In order to avoid the quenching effect by oxygen, solutions were initially nitrogen-saturated and reactions were performed in a 30 mL closed reaction vessel.

The time evolution of the concentration of each isomer was followed by gas chromatography, using a 5 m column filled with 20% squalane on chromosorb P (45−60 mesh).

Results and Discussion

Thermal isomerization of **1** has been studied in the gas phase:[1,2] the ΔH^0 and ΔS^0 values are known. On the basis of our previous study of the solvent effect on this equilibrium,[3] we can safely consider that these ΔH^0 and ΔS^0 values are also valid if the isomerization occurs in a non-dipolar solvent like CCl_4. Therefore, assuming that ΔH^0 and ΔS^0 are temperature-independent, the isomerization temperature may be deduced from the determination of the equilibrium constant after sonoisomerization. The values of ΔH^0, ΔS^0, and K, from which $T = 260 \pm 30$ K was deduced, are presented in Table 1. This T value is equal to the temperature of the bulk solution.

Table 1. Enthalpy, Entropy and Equilibrium Constant Values for the Isomerization of (1)

ΔH^0 [a]	ΔS^0 [a]	K[b]
−3012 J mol^{-1}	−2.05 J mol^{-1} K^{-1}	3.2 ± 0.5

[a] From ref 2 (temperature range: 185−275 °C). [b] From experimental measurements under ultrasonic irradiation (inducer: 1-bromobutane).

Table 2. Influence of the Vapor Pressure of the Inducer on the trans- to cis-1 Isomerization Yield

inducer	P_v (mmHg)[a]	% isomerization after 50 min
n-C_3H_7Br	68	66 ± 3
n-C_4H_9Br	18	57 ± 2
n-$C_5H_{11}Br$	5.5	49 ± 2
n-$C_6H_{13}Br$	1.7	43 ± 1
n-$C_{12}H_{25}Br$	10^{-3}	19 ± 1

[a] Calculated according to ref 5.

No isomerization was observed in the absence of RBr, even after 6 h of ultrasonic irradiation. The most widely accepted theory of transient cavitation[4] suggests that the temperature of the gas content of the cavitation bubbles at the end of collapse is very high. If we accept this conclusion, the absence of thermal isomerization observed in our case must be interpreted as a proof that the fraction of molecules of **1** reaching the intrabubble gaseous phase is very small. This result is, in some way, rather disappointing because **1** was chosen for its high volatility (P_v = 155 mmHg at 10 °C).[5] In absence of any data on the number of bubbles reaching the transient collapse during a 6 h period of time, it is not possible to explore further the quantitative interpretation of this experimental fact.

The addition of the nonvolatile radical scavenger 2,2-diphenyl-1-picrylhydrazyl (DPPH) at a very low concentration (10^{-5} mol dm^{-3}) completely inhibits the reaction. This proves that the isomerization step occurs mainly in the liquid phase. Moreover, a study of the effect of DPPH concentration on the isomerization rate leads to the conclusion that one bromine radical must be able to isomerize 8500 molecules of **1**.

The isomerization rate decreases as the vapor pressure of the various inducers decreases (see Table 2). This shows that the homolytic cleavage of RBr occurs mainly in the gas phase, during the bubble collapse.

It could appear surprising that the sonocleavage of R−Br takes place in the gas phase while the thermal isomerization of a volatile compound, i.e. **1** does not. This paradox can be explained if we remember that one bromine radical is able to isomerize 8500 molecules of **1**. Therefore, even if the sonochemical yield is very low, it can be indirectly observed since the induced isomerization plays the role of amplifier. A low yield for the direct isomerization in the gas phase, even if it occurs, would not be observed.

We are thus able to describe the reaction by the following two steps: (a) sonocleavage of R−Br in the gas

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phase due to the extreme conditions associated with transient cavitation; (b) migration of the bromine radicals into the liquid phase surrounding the collapsing bubble and reversible addition to **1** leading to isomerization.

This reaction sequence takes place in two different phases and illustrates the difficulty to obtain a quantitative interpretation of experimental facts observed in sonochemistry even in the simplest case of so-called homogeneous sonochemistry which is, in fact, not homogeneous at all.

As we previously claimed, the term homogeneous sonochemistry is misleading.[6] The acoustic field introduces spatiotemporal inhomogeneities in the medium and these inhomogeneities are at the origin of sonochemistry!

The number of papers devoted to the experimental temperature determination of a reaction induced by ultrasound is small. The pioneer work of Suslick et al.[7] gives a very high temperature value because, in the case of the sonolysis of $Fe(CO)_5$, the reaction takes place essentially in the bubble gaseous phase. Very recently, Ando et al.[8] have determined the temperature of the radical chain reaction of lead tetraacetate with β-methylstyrene induced by ultrasound and they reached the conclusion that, in their case, the temperature of the reaction is equal to the bulk temperature. The system studied by Ando et al. is different from our system because it is heterogeneous, even in absence of ultrasound.

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