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SPIN TRAPPING OF RADICALS GENERATED BY ULTRASONIC DECOMPOSITION OF ORGANOTIN COMPOUNDS

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Summary

The exposure of organotin compounds to ultrasonic radiation (55 kHz) leads to the formation of free radicals. ESR spin trapping using nitrosodurene as a spin trap was shown to be a reliable method for the detection of alkyl and aryl radicals generated during sonolysis.

Introduction

Although chemical reactions induced by intense ultrasonic waves are known for more than 50 years [1], the mechanisms of many of these reactions have not been elucidated [2–4]. Recently Riesz et al. [5,6] have successfully applied the ESR spin trapping technique [7] for the detection of free radicals produced during the sonolysis of halocarbons and water. However, aside from some product studies, only little information was available about sonochemical reactions of organometallic compounds [8–11]. Most of these reactions have been studied in aqueous solutions where $H^{\cdot}$ and $HO^{\cdot}$ radicals are formed by sonolysis. Hence, the observed transformations of the metal compounds are due to secondary reactions rather than to primary interactions with the ultrasonic waves.

We report here the results of ESR spin trapping studies of the sonolysis of organotin compounds in benzene solution. Since benzene appears to be inert towards ultrasonic radiation the observations reflect the direct, i.e. not solvent mediated interaction of ultrasound with the metal compounds.

Experimental

The organotin compounds ($Bu_3SnSnBu_3$, $Me_3SnSnPh_3$, Bu_4Sn, Et_4Sn, Me_4Sn, Ph_4Sn, Bu_2Ph_2Sn, $(PhCH_2)_3SnCl$) were available from Alfa Inorganics and used

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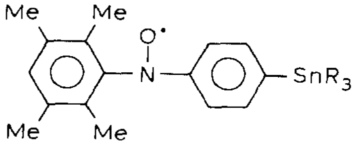
without further purification. Nitrosodurene (ND) was prepared as described in the literature [12]. Test tubes containing nitrogen-saturated dry benzene solutions of ca. 2 *M* organotin compound and 0.01 *M* ND spin trap [13] were placed in the center of a water-filled bath of a Bransonic 220 Ultrasonic cleaner (Branson; frequency 55 kHz; intensity 125 W) and sonicated for 20 minutes. The temperature of the bath did not exceed 305 K during the experiment. Precautions were taken to avoid inadvertent photolysis of the samples. The ESR spectra were recorded immediately after the sonolysis using a Varian E-104 spectrometer. All measurements were made at room temperature. Samples were prepared and degassed in a hood. A previously described computer program [14] was used for the simulation of the ESR spectra.

Results and discussion

Intense ESR signals were recorded after the sonolysis of the organotin compounds whereas no signal were detected with samples stored for 1 h at ca. 315 K but not exposed to ultrasound. Moreover, no ESR signals were obtained when benzene solutions of nitrosodurene not containing the tin compound were sonicated for 1 h. These results suggest that the observed chemical changes are solely due to the interaction of the ultrasonic waves with the tin compounds.

A typical ESR spectrum obtained after the sonolysis of hexabutylditin is shown in Fig. 1. It may be interpreted in terms of the superposition of the ESR signals of two different aminoxyl radicals: (a) The spin adduct of n-butyl radicals to ND [13]; $a_N = 13.49$, $a_H^\beta = 10.65$ (2H) G. (b) $a_N = 10.53$; $a_H^1 = 2.70$ (2H); $a_H^2 = 0.75$ (2H) G. The latter also exhibits a ^{119}Sn hyperfine splitting of 7.6 G indicating the presence of one tin nucleus per molecule (natural abundance of ^{119}Sn: 8.68%; $I = 1/2$). Even though this particular aminoxyl has not been previously reported, the coupling constants suggest a tin-substituted arylaminoxyl with a trialkyltin substituent probably in the *para* position (I). Similar results were obtained with other tin compounds (see Table 1).



(I) (R = n-butyl)

The formation of alkyl radicals from alkyltin compounds strongly suggests the sonochemical cleavage of the Sn–C (and perhaps Sn–Sn) bonds. The strongest signals were observed with butyl-, ethyl- and benzyl-tin compounds, whereas tetramethyl- and tetraethyl-tin gave only weak signals. In general tin-substituted phenyl radicals (as I for example) could also be observed.

The signal intensity was roughly $Bu_3SnSnBu_3 \gg \sim 1000 \times Me_3SnSnMe_3 \simeq Ph_3SnSnPh_3$. The formation of these radicals may be explained by the addition of tin-centered radicals to benzene, followed by spin trapping of the cyclohexadienyl addition product (Scheme 1).

ESR signals which may be assigned to the cyclohexadienylaminoxyl (II) have been recorded in some cases as well (Table 1). The nature of the oxidant is not

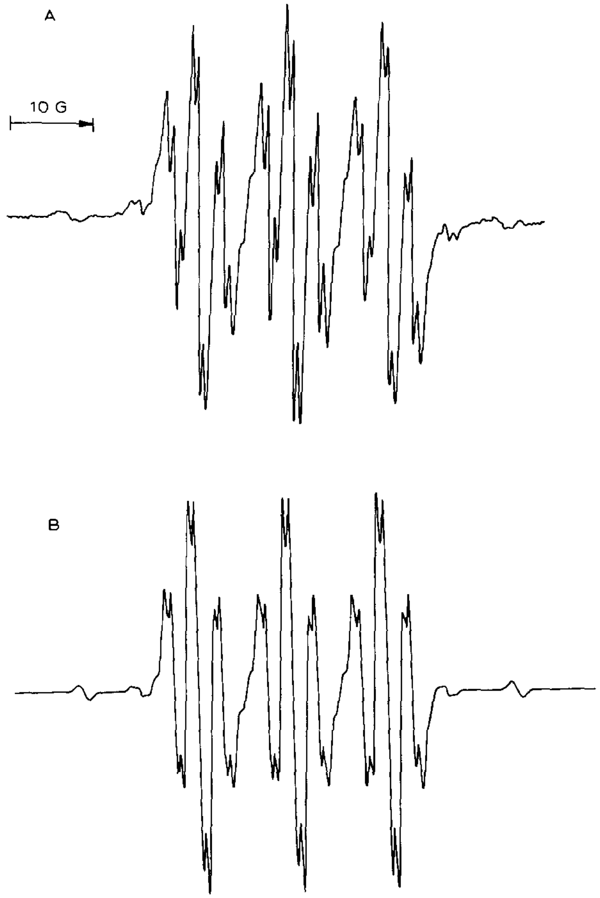


Fig. 1. (A) ESR spectrum obtained after sonolysis of hexabutylditin in benzene; (B) Computer simulation using the following coupling constants: $a_N = 10.53$ G, $a^1_H = 0.75$ G (2H), $a^2_H = 0.75$ G (2H), $a_{Sn} = 7.60$ G (linewidth: 0.67 G) for 4-$C_6H_4SnBu_2$ $a_N = 13.49$ G, $a_H = 10.65$ G (2H) (linewidth: 1.4 G).

SCHEME 1

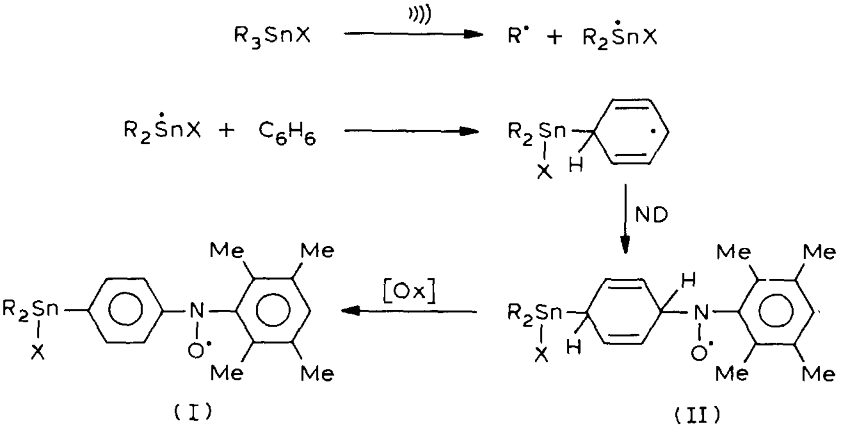
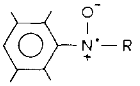
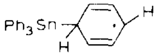


TABLE 1

SPIN ADDUCTS OF NITROSODURENE DETECTED DURING THE SONOLYSIS OF ORGANOTIN COMPOUNDS[a]



Tin compound	R	Hyperfine coupling constants		
		a_N	a_H	a_{other}
$Bu_3SnSnBu_3$	$^{\cdot}CH_2(CH_2)_2CH_3$	13.49	10.65 (2)	0.75 (2H)
	$4\text{-}C_6H_4SnBu_3$ (I)	10.53	2.70 (2)	7.60 (1Sn)
$Me_3SnSnMe_3$	$^{\cdot}CH_3$	13.7	12.9 (3)	
	$4\text{-}C_6H_4SnMe_3$ (I)	10.55	2.7 (2)	0.8 (2H)
$Ph_3SnSnPh_3$	$^{\cdot}C_6H_5$	10.1	2.8 (2)	not resolved
	$4\text{-}C_6H_4SnPh_3$	10.6	2.8 (2)	not resolved
$Sn(Bu)_2Ph_2$	$^{\cdot}CH_2(CH_2)_2CH_3$	13.5	10.7 (2)	
	$^{\cdot}CH(CH_3)_2$ [b]	13.7	7.0	
$SnMe_4$	$ND^- SnMe_3^+$	15.3		
	$^{\cdot}CH_3$	13.7	12.9 (3)	
	$^{\cdot}C_2H_5$ [c]	13.6	10.0 (2)	
$SnEt_4$	$^{\cdot}C_2H_5$	13.5	11.1	
	$4\text{-}C_6H_4SnEt_3$	10.6		not resolved
$SnPh_4$		14.3	13.3	
	$^{\cdot}C_6H_5$	10.1	2.8 (2)	
	$^{\cdot}C_2H_5$ [c]	13.6	10.1 (2)	
$Sn(CH_2C_6H_5)_3Cl$	$^{\cdot}CH_2C_6H_5$	13.5	6.5 (2H)	
	$^{\cdot}CH(C_6H_5)Sn(CH_2C_6H_5)_2Cl$	13.8	5.2 (1H)	
	$4\text{-}C_6H_4SnCl_x(CH_2C_6H_5)_{3-x}$	10.5	2.7 (2H)	0.8 (2H)

[a] All coupling constants in G; ±0.1 G; number of interacting protons in parentheses. [b] $CH(CH_3)_2I$ added. [c] CH_3CH_2I added.

known but traces of oxygen in the sample cell, aminoxyls, or the spin trap itself are the most likely candidates. In agreement with earlier attempts [15] no stable spin adducts of tin-centered radicals with nitrosodurene were detected. However, the formation of tin-centered radicals has been proven independently by the use of ethyl iodide or isopropyl iodide which are known to give alkyl radicals upon reaction with tin-centered radicals [16]. Strong ESR signals of ethyl- and isopropyl-durylaminoxyls were recorded in these cases. In order to avoid interference by the sonolysis of the alkyl iodides only short periods of sonication (< 5 min) were applied under conditions where control experiments with the alkyl iodides alone did not give rise to any detectable signals due to aminoxyls.

It is generally assumed that the chemical changes in ultrasonic reactions are caused by the phenomenon of cavitation [2–4] which leads to extremely high local temperatures and pressures as well as charge separations. In aqueous solution in the absence of any volatile solute the primary reaction is the formation of hydroxyl radicals and hydrogen atoms. This reaction takes place entirely in the gaseous phase of the cavitation space [17]. The radicals can either recombine (sometimes with the emission of sonoluminescence [18]) or diffuse into the condensed phase where they may undergo secondary reactions with the solute. We assume that the organotin compounds are a constituent of the gaseous bubble created during the sonolysis where they undergo Sn–Sn and Sn–C bond scission. The radicals thus generated react with molecules in the solvent cage or diffuse into the bulk solution where they are trapped by ND. Since no radicals were detected after 60 min sonolysis of benzene solutions of ND itself any reactions of benzene or ND in the gaseous bubble must either be reversible or devoid of radical production.

It should be noted that photolysis ($\lambda > 310$ nm) or thermolysis (refluxing benzene solutions for 30 min) gives slightly different results. Thus the photolysis of hexa-n-butylditin in the presence of ND gave n-butyldurylaminoxyl exclusively, and no n-butylaminoxyls were detected after thermolysis. Thus the signal due to the n-butyl adduct disappeared in less than 2 min at 50°C. On the other hand fairly strong ESR signals due to I were detected after thermolysis of hexa-n-butylditin.

Probably these findings reflect the different stabilities of the aminoxyl spin adducts produced rather than different reaction mechanisms. This also suggests that sonolysis is a mild method for the generation of free radicals for certain purposes.

Acknowledgment

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