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Preliminary communication

Comparison of isotope effects in reactions of monohydrosilanes

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In the course of studies on the previously reported reaction[1,2] of hydrosilanes with ozone, it has now been found that the process:

$$\geqslant\mathrm{SiH} + \mathrm{O_3} \xrightarrow{*} \geqslant\mathrm{SiOH} + \mathrm{O_2}$$

has a remarkably large deuterium isotope effect; $k_{\mathrm{rel}}(\mathrm{R_3SiH})/k_{\mathrm{rel}}(\mathrm{R_3SiD})$ equals 6.9 at 0°, where R is n-butyl. This is substantially greater than the theoretical value of 4.5 computed from the zero-point-energy effect[3] based on the Si–H and Si–D stretching frequencies of 2102.5 and 1528.2 $\mathrm{cm^{-1}}$ observed for the respective tri(n-butyl)silanes in the solvent hexane. This clearly implies the existence of a primary isotope effect and, hence, participation of the Si–H bond in a rate-determining step.

In order to ascertain the generality of this phenomenon as well as to uncover other possibly mechanistically analogous reactions of hydrosilanes, the isotope effects were determined for a number of other previously reported processes using $\mathrm{R_3SiH}$ substrates. These included reactions with chlorine[4], trityl chloride[5], nitrogen dioxide[6], and dichlorocarbene[7,8]. Values for base-catalyzed hydrolysis had already been described in the literature[9,10]. The experimental procedure was based on the gas chromatographic analysis of competition reaction mixtures of tri(n-butyl)silane, tri(n-butyl)deuteriosilane, and triphenylsilane, as appropriate in a suitable solvent with a normal n-alkane as an internal reference standard for quantitative measurements.

The results are presented in Table 1. Also shown are the signs of the reaction parameters, ρ^*, as deduced from the structure-dependent relative rate behavior. Making use of the Si–H stretching frequency correlation previously published[12] and the relationship between these frequencies and Taft σ^* parameters[13,14], one can interpret the minus (plus) sign of ρ^* as indicative of increased (decreased) development of a positive charge

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TABLE 1

ELECTRONIC AND ISOTOPE EFFECTS

$\geq$SiH reaction	Sign of ρ^* [a]	Rate (SiH)/Rate (SiD)
$+ O_3 \rightarrow \ \geq SiOH$	$-$	6.9
$+ H_2O \xrightarrow{OH^-} \ \geq SiOH$	$+$ [b]	1.2 [c], 1.4 [d]
$+ Cl_2 \rightarrow \ \geq SiCl$	$-$ [g]	1.0
$+ Ph_3CCl \rightarrow \ \geq SiCl$	$+$	1.5
$+ NO_2 \rightarrow \ \geq SiOH$	$-$	1.2
$+ :CCl_2 \rightarrow \ \geq SiCCl_2H$	$-$ [e]	1.23 [f]

[a] See text for interpretation. [b] Ref. 16 gives $\rho^* = +4.27$ for best linear plot. [c] Ref. 9, at 25°. [d] Ref. 10, 25°. [e] Ref. 8 gives $\rho^* = -0.632$. [f] T.F. Jula, private communication estimated approx. 1.1 from infrared analyses. [g] Ref. 17 gives $\rho^* = -4.2$.

on silicon in the transition state or, alternatively of electrophilic (nucleophilic) attack in the rate-determining step.

It is evident from inspection of Table 1 that the mechanism of the hydrosilane–ozone reaction must be quite different from that of any of the other tabulated reactions, all of which show only small or, possibly, no (in the case of chlorine) deuterium isotope effect, even though the sign of ρ^* may vary.

Since the initial ozone runs used 3–4% ozone in oxygen as the reagent, the possibility existed that the oxygen content might be responsible for the abnormally high isotope effect through catalytic autoxidation. Such had been found to occur in the ozonization of aldehydes[15]. However, this was ruled out when studies here with ozone in argon as the reactant produced at the same high isotope effect.

The detailed mechanistic rationale for the unusual reaction with ozone is the subject for a separate publication.

EXPERIMENTAL

Analyses were performed by VPC on a 100 ft. 0.1 in. DC-550 coated capillary column in a Perkin–Elmer Model 226 Chromatograph. Reaction mixtures contained a suitable n-alkane as an internal standard.

For the oxygen-free ozone studies, ozone was adsorbed onto silica gel at dry ice temperatures and then eluted by warming slightly in a stream of argon.

Competition studies were run with approximately 0.2–0.3 ml of each of two trisubstituted monohydrosilanes to be compared and 0.1–0.2 of the internal standard in 10 ml of an appropriate solvent. The experimental conditions, such as temperature, solvent, and internal standard for each of the reactants of this study are presented in Table 2. Because of the limited number of compounds here examined, it was felt that only the sign of the reaction parameter, ρ^*, should be reported at this time.

TABLE 2

EXPERIMENTAL CONDITIONS FOR HYDROSILANE REACTIVITY STUDIES WITH VARIOUS REAGENTS[a]

Reactant	Solvent	Temperature (°C)	Internal standard (n-alkane)
Ph_3CCl	CH_2Cl_2	23	C_{11}
NO_2	CH_2Cl_2	19	C_{11}
Cl_2	CH_2Cl_2	0	C_{11}
O_3	Hexane	0	C_{11}, C_{16}
$:CCl_2$ [b]	Benzene	80	C_{11}

[a] Principal hydrosilane substrates used in the competition studies were n-Bu_3SiH, n-Bu_3SiD and Ph_3SiH.
[b] Generated from $PhHgCCl_2Br$ by the method of ref. 8.

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