278. Secondary Deuterium Isotope Effect in an Electrophilic Aromatic Substitution - Protodesilylation of Trimethylphenylsilane

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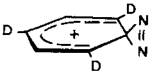
Summary

Reaction rates for the protodesilylation of trimethylphenylsilane and of [2,4,6-$^2H_3$]-trimethylphenylsilane by $HClO_4$, were measured in aqueous methanol (2:5, *v/v*) and the secondary deuterium isotope effect for the reaction was found to be $k_H/k_{D_3} = 0.79$. The magnitude of the observed isotope effect supports a mechanism in which the rate-determining step is the proton transfer from the hydronium ion to the silane to form a σ-intermediate.

Introduction. - Recently we measured secondary deuterium isotope effects in reactions of benzenediazonium tetrafluoroborate, and these were used to differentiate between two possible reaction intermediates for the N_α-N_β rearrangement reaction that accompanies the dediazoniation [1]: the phenyl cation/N_2 molecule pair and the benzenespirodiazirine cation (**1**). We concluded that the observed isotope effect on the rearrangement of [2,4,6-$^2H_3$]-benzenediazonium tetrafluoroborate (k_H/k_{D_3} = 1.42) definitely excludes structure **1** as an intermediate, since for rate determining formation of **1** an isotope effect k_H/k_{D_3} smaller than unity is expected.



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The C,H-(C,D)-bonds are perpendicular to the π-system where the positive charge is distributed; no hyperconjugative stabilization is possible [2], and therefore only a small inductive inverse secondary deuterium isotope effect should be observed[1]).

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[1]) The positive inductive effect of a heavy isotope relative to a light one can be explained [3] by vibrational anharmonicity and has been shown for hydrogen isotopes in many cases, *e.g.* solvolysis reactions of benzhydryl chloride [4], the equilibrium formation of triphenylcarbenium ions [5], brominations of alkenes [6], the basicity of aniline [7], azo-couplings [8], *etc.*

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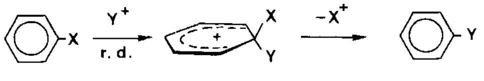
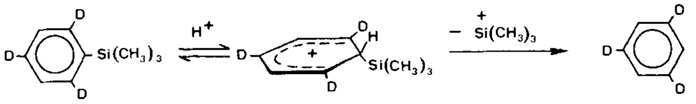
Surprisingly, no data are available for secondary deuterium isotope effects in a suitable model electrophilic aromatic substitution which proceeds by rate determining formation of a σ-complex or *Wheland*-type intermediate similar to **1**. In spite of the multitude of kinetic measurements with isotopically labelled compounds [9], to the best of our knowledge, no β- and more remote secondary deuterium isotope effects for reaction (1) are known. *Olah et al.* [10] determined the isotope effects for the nitration of deuterated benzene, toluene and fluorobenzene and obtained k_H/k_D values between 0.85 and 0.90, but in each case the leaving group X was also a ^{2}H-atom, and therefore an α-secondary deuterium isotope effect[2]) was superimposed. Kinetic secondary deuterium isotope effects were also determined for the formation of phenylcarbenium ions [4] [13] and of phenylammonium ions [14], but in both cases the cationic centre is not on a ring C-atom, and the reaction is not an electrophilic aromatic substitution.



(1)

In the absence of satisfactory isotope effect data, we measured the secondary deuterium isotope effect in an electrophilic aromatic substitution. The protodesilylation of trimethylphenylsilane[3]), the mechanism of which has been thoroughly investigated by *Eaborn et al.* [15], was chosen as the model reaction (2).



(2)

[^{2}H$_3$]-**2** [^{2}H$_3$]-**3**

Proton transfer to the silane is the slow step, and the loss of proton from the σ-complex **3** is slower than the loss of the trimethylsilyl group [15]. Therefore the secondary deuterium isotope effect measured for the protodesilylation (2) should be a good estimate of the effect expected for the N_α-N_β rearrangement accompanying the dediazoniation reaction, if it were to proceed through the benzenespirodiazirine cation **1**.

Results and discussion. - The reaction rate for the protodesilylation of trimethylphenylsilane (**2**) and of the [2,4,6-^{2}H$_3$]-compound ([^{2}H$_3$]-**2**) by perchloric acid was measured in aqueous methanol (2:5, *v/v*) at 50° by following the disappearance of the reactant by UV. spectroscopy. Good first-order kinetics were observed for at least 85% reaction. The rates and the secondary deuterium isotope effect are shown in *Table 1*.

The [2,4,6-^{2}H$_3$]-silane reacts faster than the protio compound, and the magnitude of the isotope effect fits the expectation for the formation of the σ-complex **3**

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[2]) α-Secondary deuterium isotope effects both larger and smaller than unity have been observed in electrophilic aromatic substitutions [10–12]. An $sp^2 \rightarrow sp^3$ rehybridization at the C(α)-atom should result in a $k_H/k_D < 1$, while a hyperconjugative stabilization of the positive charge in the σ-intermediate by the C,H_α-(C,D_α-)bond should give a $k_H/k_D > 1$. These two effects may cancel.

[3]) The author thanks Professor *R. W. Hoffmann*, Philipps-Universität, Marburg, Germany, who, after a discussion of deuterium isotope effects in dediazoniations, suggested the protodesilylation as a model reaction.

Table 1. *Rate constants and the secondary deuterium isotope effect for the protodesilylation of trimethylphenylsilane* (**2**) *and [2,4,6-$^2H_3$]-trimethylphenylsilane ([$^2H_3$]-*__2__*) by $HClO_4$ in aqueous methanol*[a]) *at 50°*

Compound	k[b]) × 10^5 [s^{-1}]	k_H/k_{D_3}[b])
2	1.81 ± 0.27[c])	
[$^2H_3$]-**2**	2.29 ± 0.44	0.79 ± 0.19[c])

[a] Reaction medium: 9.2M $HClO_4$ in water/0.007M silane in methanol 2:5, *v/v*.

[b] Average of six measurements. The isotope effect is uncorrected. The deuterium content was found to be 97.8% $^2H_3$.

[c] Standard deviation.

in a slow step, where the small positive inductive effect of deuterium, relative to protium is operating. The observed isotope effect is not in accordance with an alternative desilylation mechanism [16] that proceeds by partial formation of aryl anions in the rate determining step. Such a mechanism would require an isotope effect slightly larger than unity [13]. The isotope effect determined for reaction (2) supports the previous argument [1] that the isotope effect in the N_α-N_β rearrangement during dediazoniation of [2,4,6-$^2H_3$]-benzenediazonium ions excludes structure **1** as an intermediate for the rearrangement.

The source of the observed secondary deuterium isotope effect in the protodesilylation reaction (2) can be elucidated by the following analysis. From absolute rate theory and statistical mechanics *Bigeleisen* has derived an equation for calculating the isotope effect on rate [17]. This equation was further transformed and simplified by *Streitwieser et al.* [18], who obtained the expression (3)[4], where ν_{Hi} and $\nu^{\ddagger}_{Hi}$ are frequencies for the C,H-vibrations in the ground state and in the transition state, respectively. There is no problem to assign reasonable values to

$$\frac{k_H}{k_D} \simeq \pi_i \, e^{\frac{0.187}{T}(\nu_{Hi} - \nu^{\ddagger}_{Hi})} \tag{3}$$

the three C,H-stretching and -bending fundamentals of trimethylphenylsilane [20] [21]. It is harder to assign frequencies to the three fundamental vibrations in the σ-complex-like transition state. Since, to the best of our knowledge, no satisfactory IR. spectra of σ-complexes such as **3** are known[5], nitrobenzene, where there is also partial positive charge at the *o*- and *p*-positions, was taken as a crude model. The fundamental vibrations of nitrobenzene are known [21]. *Table 2* lists the frequencies corresponding to the fundamental C,H-vibrations of the ground state and the model transition state, as well as the calculated multiplicative contributions of these vibrations to the overall isotope effect.

From the calculation presented in *Table 2* the increase in the out-of-plane bending frequency in the transition state must be the major contribution to the total isotope effect. The decrease in the in-plane bending frequency, and the increase

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[4] The harmonic oscillator approximation was used and the frequencies of the deuteriated compound were assumed to be reduced by 1/1.35 [19].

[5] The IR. spectra of proton addition complexes of benzene (with $AlCl_4^-$, $AlBr_4^-$ and $GaCl_4^-$ as counter-ions) in the solid state were recorded in the region of 400-2000 cm^{-1} [26]; thus the C,H-stretching frequencies for the complex being unknown, nitrobenzene was preferred as the model transition state for the desilylation.

Table 2. *Frequencies and calculated isotope effects for the formation of σ-complex* 3

	Frequencies [cm^{-1}]		Contribution
	G.S.	T.S. (est.)	to k_H/k_D
Ar, H-stretch	3050	3079	0.983
Ar, H-bending in plane	1100	1068	1.019
Ar, H-bending out-of-plane	715	792	0.956
		Total:	0.958
		Total $^2H_3$[a]):	0.88

[a]) Assuming the effects per $^2H_3$ to be additive.

in the stretching frequency are relatively small, and these two contributions to the total isotope effect cancel out in the system under study. The estimated total isotope effect for the formation of σ-complex 3, $k_H/k_{D_3} = 0.88$ fits the observed value ($k_H/k_{D_3} = 0.79$) fairly well, and lends further support to the postulated mechanism of protodesilylation [15].

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Experimental Part

Trimethylphenylsilane was prepared by a modified procedure of *Eaborn* [22]. Chlorotrimethylsilane (1.91 g) was boiled under reflux for 7 h with the *Grignard* reagent prepared from bromobenzene (3.00 g) and magnesium (0.47 g) in ether (6 ml). Hydrolysis, followed by extraction with ether (3×50 ml), drying of the ethereal layer and distillation yielded trimethylphenylsilane (2.01 g, 70%). The product was redistilled and further purified on a silica column (CH_2Cl_2). - NMR. ($CDCl_3$): 0.31 (*s*, 9 H); 7.25-7.62 (*m*, 5 H).

[2,4,6-$^2H_3$]-Bromobenzene was prepared from [2,4,6,*N*,*N*-$^2H_5$]-aniline (6.0 g) [23] by a *Sandmeyer* reaction, as described in [24]. Yield 6.35 g (64%). - NMR. ($CDCl_3$): 7.22 (*s*).

[2,4,6-$^2H_3$]-Trimethylphenylsilane was prepared from [2,4,6-$^2H_3$]-bromobenzene in the same way as the protio compound described above. - NMR. ($CDCl_3$): 0.26 (*s*, 9 H); 7.34 (*s*, 2 H). The deuterium content was found to be 97.8% $^2H_3$.

Kinetic measurements. A procedure modified from [25] was used. Two stock solutions were made: (*a*) 7×10^{-3} mol/l silane in methanol (*Merck*, für Spektroskopie), and (*b*) 60% $HClO_4$ (9.2 M) in water. For each measurement 5 ml of solution *a* and 2 ml of solution *b* were mixed and thermostated in stoppered 1 cm quartz UV. cells at 50.0°. UV. spectra were recorded (relative to methanol) at definite time intervals and the disappearance of the silane was monitored at 264 nm. 'Infinity' values were obtained from samples of the reaction mixtures kept in sealed tubes at 50° for a period equivalent to 10 half-lives. A protio and a deuteriated silane sample were always run simultaneously. Plots of ln ($A_t - A_\infty$) *vs.* t were linear for *ca.* 85% reaction.

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