Acidic proton in trichlorosilane? Computations match experiment & reveal surprising mechanism

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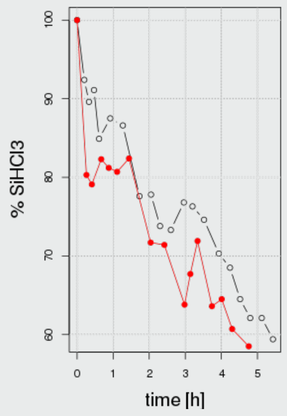
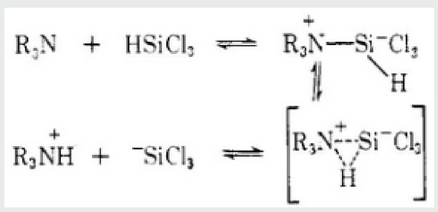
Introduction

We use DFT calculations to investigate processes involved in amin-catalysed H/D-exchange in trichlorosilane.
Bernstein [1] reported diminuition of the ^{1}H-Si-NMR signal upon adding free base to a 1:1 mix of trichlorosilane and tri-n-butylamine deuteriochloride in dichloromethane at 30 K:

$$SiHCl_3 + DNBu_3^+ \xleftrightarrow[Cl^-,DCM]{NBu_3} SiDCl_3 + HNBu_3^+$$

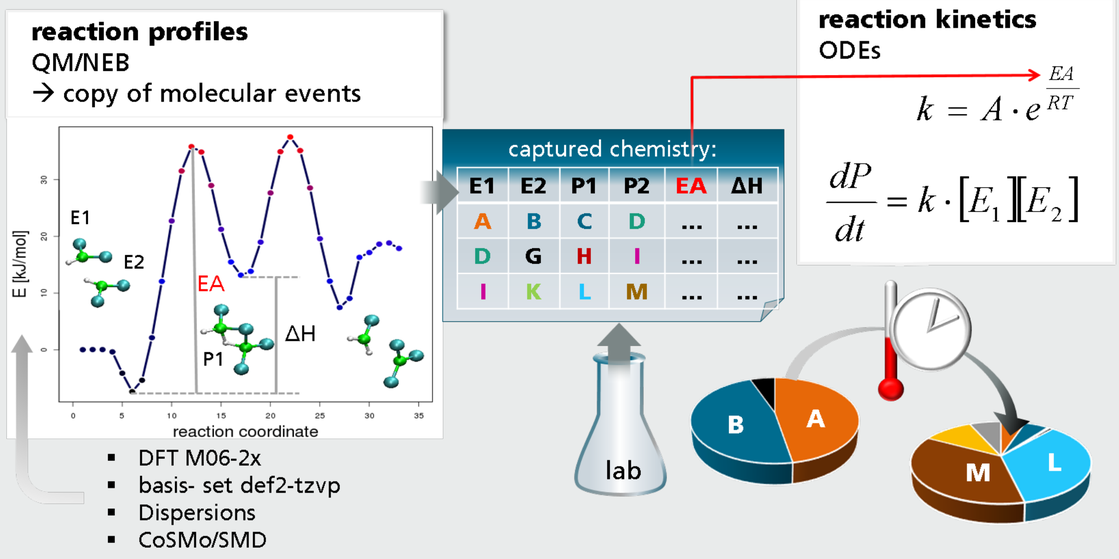


He also proposed that the transfer of the proton from Si to N proceed via an intermediate donor-acceptor adduct:



Method

- setup geometries for reaction paths manually
- reduce computational cost: butyl-groups substituted for methyl
- run nudged elastic band calculations in dichloromethane
- from energy profiles determine barrier EA and approximate ΔE for ΔH
- predict kinetic behaviour by solving ODEs derived from key figures and initial conditions



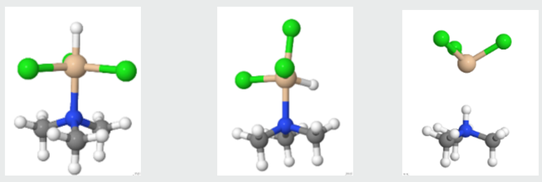
Elementary Steps

	reactant(s)	product(s)	comment	EA	ΔH
1a	$NR_3 + SiHCl_3$	$R_3N{-}SiHCl_2{-}Cl$	C_m, staggered	0.1	-56
1b	$NR_3 + SiHCl_3$	$R_3N - SiCl_3{-}H$	C_{3v}	0.1	-28
1c	$NR_3 + SiHCl_3$	$R_3N \cdot HSiCl_3$	vdW pair	0.1	-5
1d	$HNR_3^+ + SiHCl_3$	$R_3NH^+ \cdot Cl_3SiH$	vdW pair 1	0.1	-17
1e	$HNR_3^+ + SiHCl_3$	$R_3NH^+ : Cl_3SiH$	vdW pair 2	0.1	-15
2a	$R_3N{-}SiHCl_2{-}Cl$	$R_3NH^+ \cdot SiCl_3^-$	ion pair	92	56
2b.1	$R_3N{-}SiHCl_2{-}Cl$	$R_3N{-}SiHCl_2{-}Cl^*$	C_m, eclipsed	36.1	36
2b.2	$R_3N{-}SiHCl_2{-}Cl^*$	$R_3NH^+ \cdot SiCl_3^-$	ion pair	35.0	2.4
2c	$R_3N{-}SiHCl_2{-}Cl$	$R_3NH^+ \cdot SiCl_3^-$	ion pair	65.5	38.5
2d	$R_3N \cdot HSiCl_3$	$R_3NH^+ \cdot SiCl_3^-$	ion pair	25	-20
3a	$R_3NH^+ \cdot SiCl_3^-$	$R_3NH^+ \cdot Cl_3Si^-$	ions rotated	3.1	- 25
3b	$R_3NH^+ \cdot SiCl_3^-$	$R_3NH^+ + SiCl_3^-$	ions sep.	45.1	45
4a	$R_3NH^+ \cdot SiCl_3^- + DNR_3^+$	$HNR_3^+ + Cl_3Si^- \cdot DNR_3^+$	lat. displ.	0.1	0
4b	$R_3NH^+ \cdot SiCl_3^- + DNR_3^+$	$HNR_3^+ + Cl_3SiD \cdot NR_3$	lat. displ.	0.1	0
4c	$R_3NH^+ \cdot SiCl_3^- + DNR_3^+$	$HNR_3^+ \cdot Cl_3SiD + NR_3$	lat. displ.	0.1	0

exemplary for H; since chemisty is the same for deuterium, results may be transferred for setting up the ODEs

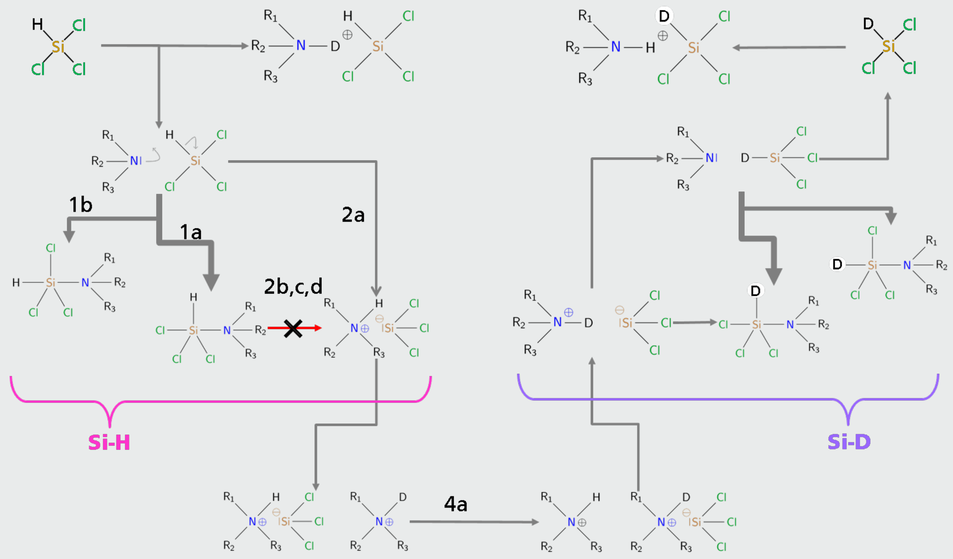
Results

principal contacts in accordance with expectations:

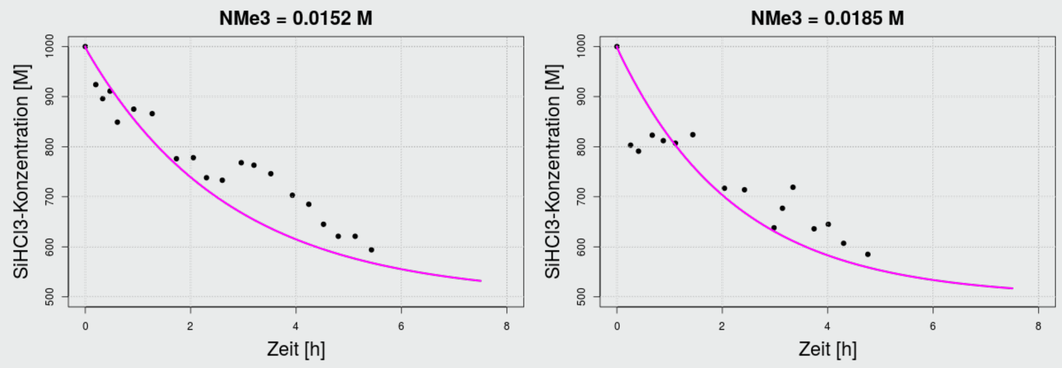


C_{3v}-symmetry C_m-symmetry ion pair

continuous pathway to products found:

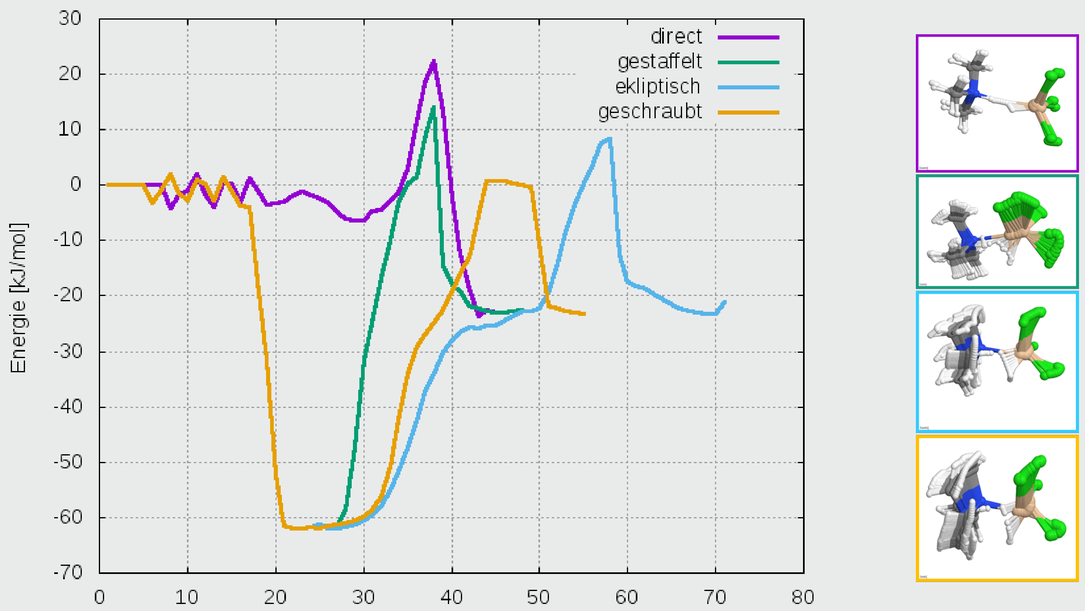


decay well reproduced:



surprising intermediate:

- postulate requires prohibitive energy barrier
- calculations favor direct deprotonation



Conclusion

- experimental findings well reproduced
- indication of acidic nature of hydrogen in trichlorosilane

Bibliography

[1] Stanley C. Bernstein.
On the mechanism of interaction between tertiary amines and trichlorosilanes.
J. Am. Chem. Soc., 92:699–700, 1969.

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