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MASTER

Disproportionation of Trimethylsilyl Radicals to a Silaolefin in the Liquid Phase

Becky J. Cornett, Kwang Yul Choo and Peter P. Gaspar*

Department of Chemistry
Washington University
Saint Louis, Missouri 63130

Abstract

Despite previous reports, including our own, trimethylsilyl radicals in the liquid phase undergo disproportionation as well as recombination, in ratio 1 : 5. The CH_2=$SiMe_2$ formed by disproportionation is trapped by alcohols.

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DISCLAIMER

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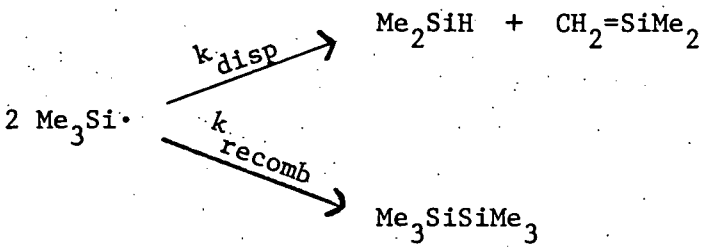
Sir:

Until very recently the disproportionation of trimethylsilyl radicals to the sila-olefin 2-methyl-2-silapropene was considered to be a minor process compared to radical recombination.[1]



We have reexamined the self-reactions of trimethylsilyl radicals in solution, prompted by the high ratio of disproportionation to recombination, $k_{disp} : k_{recomb} = 0.48$ found in the gas phase by Tokach and Koob.[2] We find that disproportionation is also an important process for trimethylsilyl radicals in the liquid phase.

When trimethylsilyl radicals are generated by photolysis of tert-butyl peroxide in solutions of trimethylsilane,[3] the disappearance of $Me_3Si\cdot$ as monitored by kinetic esr spectroscopy is a rapid process, second-order in the concentration of $Me_3Si\cdot$.[4,5]

$$Me_3COOCMe_3 + h\nu \longrightarrow 2\ Me_3CO\cdot$$

$$Me_3CO\cdot + Me_3SiH \longrightarrow Me_3COH + Me_3Si\cdot$$

$$2\ Me_3Si\cdot \longrightarrow \text{products}$$

Based on the observation of hexamethyldisilane and tert-butanol as the sole reaction products at the short reaction times of the kinetic studies, radical recombination was believed to be the exclusive mode of self-reaction for tri-

methylsilyl radicals.[5] A third product found at longer irradiation times, tert-butoxytrimethylsilane $Me_3COSiMe_3$, was believed to be a secondary product,[5] but we now know that it is formed by trapping of the disproportionation product by tert-butanol.[6]

$$Me_3COH + CH_2{=}SiMe_2 \longrightarrow Me_3COSiMe_3$$

In the kinetic studies tert-butanol is generated in situ, and thus initially there is no trapping reagent present capable of converting the sila-olefin to a stable low molecular weight product.[7] We have now established that tert-butoxytrimethylsilane is an early product when trapping reagent is present and is formed from addition of alcohol to sila-olefin. Several alternative mechanisms for formation of $Me_3COSiMe_3$ have been eliminated.

In the presence of excess tert-butanol the product ratio $Me_3COSiMe_3$: $Me_3SiSiMe_3$ = 0.19 ± 0.05 remained constant with irradiation time. That 2-methyl-2-silapropene was being trapped was demonstrated by use of Me_3COD either generated in situ from Me_3SiD or added in excess.

$$Me_3COD + CH_2{=}SiMe_2 \longrightarrow Me_3COSiMe_2CH_2D$$

Formation of this monodeuterated tert-butoxytrimethylsilane was established by pmr and mass spectroscopy. There is a scatter in the quantitative results covering a range of incorporation from 0.3 to 0.8 deuterons per molecule.[8] Thus the labelling experiments do not exclude contributions from additional sources of tert-butoxytrimethylsilane. Three such sources have been considered.

1. Attack by tert-butoxy radicals on hexamethyldisilane

$$Me_3CO\cdot + Me_3SiSiMe_3 \longrightarrow Me_3COSiMe_3 + Me_3Si\cdot$$

has been rendered unlikely by the absence of either product when tert-butoxy

radicals were generated in hexamethyldisilane.[5]

2. Induced decomposition of tert-butyl peroxide

$$Me_3Si\cdot + Me_3COOCMe_3 \longrightarrow Me_3COSiMe_3 + Me_3CO\cdot$$

can also be ruled out as a source of tert-butoxytrimethylsilane, since the presence of tert-butanol is required for its formation. Irradiation of mixtures of tert-butyl peroxide, trimethylsilane and methanol yields methoxytrimethylsilane and hexamethyldisilane as products, with only traces of tert-butoxytrimethylsilane.[9] Thus the alkoxysilane arises from reaction of a silicon-containing intermediate with an alcohol.

3. A remaining possibility was that it is the trimethylsilyl radical itself that reacts with an alcohol molecule to form an alkoxysilane via an unconventional radical complex that could act as a hydrogen atom donor in a chain process.[10]

$$Me_3Si\cdot + ROH \longrightarrow \underset{\displaystyle H}{[R\text{-}O\cdots SiMe_3]} \xrightarrow{Me_3SiH} ROSiMe_3 + H_2 + Me_3Si\cdot$$

A very low yield (<2%) of hydrogen speaks against this interesting process.

Since positive evidence for the formation of $CH_2{=}SiMe_2$ is given by the trapping experiments with deuterated tert-butanol, we believe that the disproportionation of trimethylsilyl radicals in solution is established. The observed product ratio $Me_3COSiMe_3$: $Me_3SiSiMe_3$ = 0.2 is insensitive to variation of alcohol concentrations above 10 mole % and thus may be equated with the ratio of bimolecular rate constants for disproportionation and recombination of trimethylsilyl radicals. Since the recombination rate is nearly at the diffusion-controlled limit,[5] the disproportionation is astonishingly rapid,[11] perhaps due to stabilization of the transition state by the incipient carbon-silicon pi-bond.

$$Me_3Si\cdot + H\text{-}CH_2\text{-}\dot{S}iMe_2 \longrightarrow [Me_3Si\cdots H\cdots CH_2\cdots SiMe_2]^{\neq} \longrightarrow Me_3SiH + CH_2{=}SiMe_2$$

Facile disproportionation of trimethylsilyl radicals may therefore be taken as indirect evidence for substantial pi-bonding in the sila-olefin.

A final point of interest is an increase at long irradiation times (>12 hr) of the yield of $Me_3COSiMe_3$ and a concomitant decrease in the yield of $Me_3SiSiMe_3$. Trapping experiments with labelled alcohol indicate that photolysis of hexamethyldisilane is another route to 2-methyl-2-silapropene. This has also been observed by Boudjouk and Koob in the gas phase.[12]

$$Me_3SiSiMe_3 + h\nu \longrightarrow Me_3SiH + CH_2{=}SiMe_2$$

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References and Footnotes

1. A ratio $k_{disp} : d_{recomb} = 0.046$ has been quoted without experimental details: O.P. Strausz, L. Gammie, G. Theodorakoupolos, P.G. Mezey, I.G. Csimadia, J. Amer. Chem. Soc., 98, 1624 (1976).
2. S.K. Tokach and R.D. Koob, J. Phys. Chem., 83, 774 (1979); see also S.K. Tokach and R.D. Koob, "Trimethylsilyl Radical: H-Abstraction and Disproportionation Reactions," abstract, XIII Organosilicon Symposium, University of Michigan, March 30-31, 1979.
3. P.J. Krusic and J.K. Kochi, J. Amer. Chem. Soc., 91, 3938 (1969).
4. P.T. Frangopol and K.U. Ingold, J. Organometal. Chem., 25, C9 (1970); C.B. Watts and K.U. Ingold, J. Amer. Chem. Soc., 94, 491 (1972).
5. P.P. Gaspar, A.D. Haizlip and K.Y. Choo, J. Amer. Chem. Soc., 94, 491 (1972).
6. Addition of alcohols to sila-olefins is now a well-known reaction; L.E. Gusel'nikov, N.S. Nametkin and V.M. Vdovin, Accts. Chem. Res., 8, 18 (1975).
7. In the gas phase no low molecular weight products have been found from $CH_2{=}SiMe_2$ at room temperature in the absence of trapping reagent; S. Tokach, P. Boudjouk and R.D. Koob, J. Phys. Chem., 82, 1204 (1978). At high temperatures dimers are formed; see reference 6.
8. These are strictly lower limits. The mass spectrometric deuterium assay of tert-butoxytrimethylsilane will be discussed in a full report of this work.
9. Control experiments showed that exchange of alkoxy groups did not occur for the product methoxytrimethylsilane nor for the recovered tert-butyl peroxide.
10. This mechanistic possibility was suggested by the observation of esr spectra by J.F.S. Wan and K.Y. Choo indicative of addition of silyl radicals to siloxanes; private communication from Professor Wan.

11. It has been pointed out (reference 1) that hydrogen atom abstraction from $Me_3Si\cdot$ must be $>10^5$ as rapid as abstraction from Me_4Si for disproportionation of trimethylsilyl radicals to be competetive with radical recombination.

12. P. Boudjouk and R.D. Koob, "On the Photolysis of Disilanes as a Source of Silaethylenes," abstract, XIII Organosilicon Symposium, University of Michigan, March 30-31, 1979. These workers employed 148 nm radiation, while in our experiments unfiltered low- and medium-pressure mercury lamps are used; our findings were also presented in an abstract to this symposium; P.P. Gaspar and B.J. Cornett, "Disproportionation of Silyl Radicals to Silenes in the Liquid Phase."