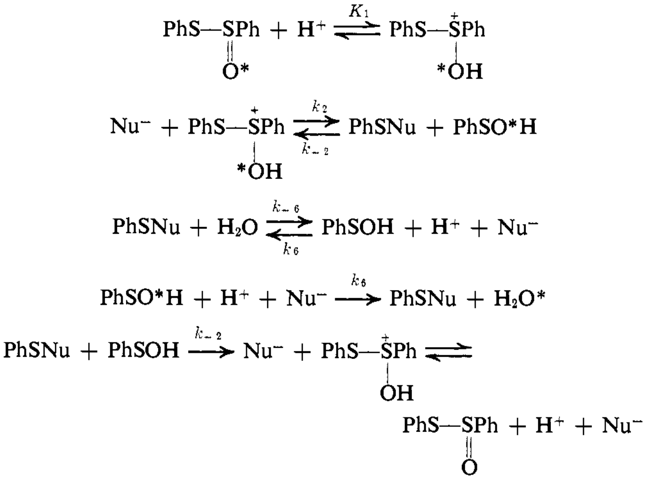
mental first-order rate constants for exchange, k_{ex}, values of (k_α/k_{ex}) are also tabulated, where k_α represents the first-order rate constant for racemization of (+)-**1** under the same reaction conditions.[2]

Acid- and nucleophile-catalyzed exchange of oxgyen-18 in **1**-^{18}O presumably proceeds by the mechanism shown in the following equations



$$\mathrm{PhS{-}\underset{\underset{\displaystyle O^*}{\|}}{S}Ph + H^+ \overset{K_1}{\rightleftharpoons} PhS{-}\underset{\underset{\displaystyle {}^*OH}{|}}{\overset{+}{S}}Ph}$$

$$\mathrm{Nu^- + PhS{-}\underset{\underset{\displaystyle {}^*OH}{|}}{\overset{+}{S}}Ph \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} PhSNu + PhSO^*H}$$

$$\mathrm{PhSNu + H_2O \underset{k_6}{\overset{k_{-6}}{\rightleftharpoons}} PhSOH + H^+ + Nu^-}$$

$$\mathrm{PhSO^*H + H^+ + Nu^- \xrightarrow{k_6} PhSNu + H_2O^*}$$

$$\mathrm{PhSNu + PhSOH \xrightarrow{k_{-2}} Nu^- + PhS{-}\underset{\underset{\displaystyle OH}{|}}{\overset{+}{S}}Ph \rightleftharpoons PhS{-}\underset{\underset{\displaystyle O}{\|}}{S}Ph + H^+ + Nu^-}$$

This mechanism predicts k_{ex} should be given by the expression in eq 5, and (k_α/k_{ex}) by eq 6. Within

$$k_{ex} = \frac{k_2K_1[\mathrm{H^+}][\mathrm{Nu^-}]}{1 + \left\{\dfrac{k_2K_1}{k_6}\,\dfrac{k_{-2}[\mathbf{1}]}{k_{-6}[\mathrm{H_2O}]}\right\}^{1/2}} \tag{5}$$

$$(k_\alpha/k_{ex}) = 1 + \left(\frac{k_2K_1}{k_6}\right)^{1/2}\left(\frac{k_{-2}}{k_{-6}[\mathrm{H_2O}]}\right)^{1/2}[\mathbf{1}]^{1/2} \tag{6}$$

experimental error k_{ex} is proportional to the first power of both hydrogen ion and nucleophile concentrations, as required by eq 5. The runs at different initial thiolsulfinate concentrations with n-Bu$_2$S as catalyst show that (k_α/k_{ex}) does depend on thiolsulfinate concentration, although the dependence, particularly at higher [**1**], is apparently somewhat more pronounced than the half-power dependence predicted by the mechanism. This apparently arises because the rate of acid- and nucleophile-catalyzed disproportionation[5] of **1** is not too much slower[6] than the rate of exchange, especially at the highest thiolsulfinate concentrations.[7]

The really important result here is what the values of (k_α/k_{ex}) suggest about the relative reactivity of PhSNu toward PhSOH and H$_2$O, steps k_{-2} and k_{-6}, respectively. Thus using the data for n-butyl sulfide as catalyst at the lowest thiolsulfinate concentration (0.0125 M), where there are no complications from the disproportionation of **1**,[6] $(k_2K_1/k_6)(k_{-2}/k_{-6}[\mathrm{H_2O}])$ is calculated to be 9×10^3. Since there is no reason to believe that k_2K_1/k_6 should be significantly greater than unity, and since in 60% dioxane $[\mathrm{H_2O}] \cong 20$ M, this suggests that $(k_{-2}/k_{-6}) \geqq 1.8 \times 10^5$. In other words, benzenesulfenic acid (PhSOH) is over 100,000 times more reactive as a nucleophile toward PhS-S$^+$(n-Bu)$_2$ than is water. It is also presumably much more reactive than water toward PhSBr and somewhat more reactive than water toward PhSCl.

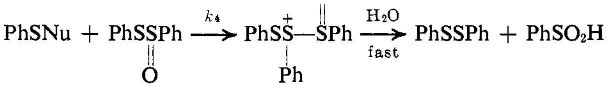
These results provide an explanation of why thiolsulfinates are invariably the first isolable product of the hydrolysis of reactive sulfenyl derivatives in water.[8] Since $k_{-2} \gg k_{-6}$, as soon as any PhSOH is formed by hydrolysis of PhSNu it reacts with some of the remaining PhSNu faster than the latter undergoes hydrolysis. Thus the inability to isolate sulfenic acids from the hydrolysis of sulfenyl derivatives may be less a matter of their inherent instability than of their high nucleophilic reactivity toward such sulfenyl derivatives.

John L. Kice,[9] James P. Cleveland[10]
Department of Chemistry, Oregon State University
Corvallis, Oregon 97331

Received May 1, 1970

---

(7) The rate-determining step of the acid- and nucleophile-catalyzed disproportionation[5] is given by



$$\mathrm{PhSNu + Ph\underset{\underset{\displaystyle O}{\|}}{S}SPh \xrightarrow{k_4} PhS\underset{\underset{\displaystyle Ph}{|}}{\overset{+}{S}}{-}\overset{\overset{\displaystyle O}{\|}}{S}Ph \xrightarrow[\text{fast}]{H_2O} PhSSPh + PhSO_2H}$$

Occurrence of this reaction siphons off some PhSNu that would otherwise undergo hydrolysis to PhSOH, which latter species would then yield unlabeled **1**. Although the exact kinetics of the situation are too complex to be amenable to simple analysis, it is evident, since the rate of the disproportionation in 60% dioxane is proportional to $[\mathbf{1}]^{3/2}$,[6] that the fraction of PhSNu prevented from undergoing eventual return to unlabeled **1** in this way will be larger the higher the concentration of **1**, thus causing (k_α/k_{ex}) to increase more rapidly with thiolsulfinate concentration than predicted by eq 6.

(8) E. Vinkler and F. Klivenyi, *Acta Chim. Acad. Hung.*, 22, 345 (1960).

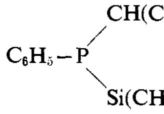
(9) To whom correspondence should be addressed at the Department of Chemistry, University of Vermont, Burlington, Vt. 05401.

(10) National Institutes of Health Postdoctoral Fellow, 1969–1970.

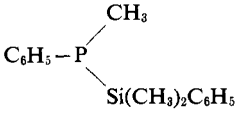
Barrier to Pyramidal Inversion in Silylphosphines[1]

Sir:

In contrast to the planar nitrogen atom in silylamines,[2] the phosphorus atom in trisilylphosphine possesses a normal pyramidal geometry characteristic of other phosphines.[3] However, we have found that the barrier to pyramidal inversion in silylphosphine **1** has the remarkably low value of $\Delta G^{\ddagger}{}_{62} = 18.9$ kcal/mol.[4] This observation demonstrates that a pronounced stabilization of the planar (relative to the pyramidal) geometry is a general phenomenon in molecules having silicon bonded to an inversion center, and not one which is restricted to the first-row elements.[6,7]



1



2

---

[1] This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

[2] K. Hedberg, *J. Amer. Chem. Soc.*, 77, 6491 (1955); E. A. V. Ebsworth, J. R. Hall, M. J. MacKillop, D. C. McKean, N. Sheppard, and L. A. Woodward, *Spectrochim. Acta*, 13, 202 (1958); G. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Struct.*, 4, 215 (1969); L. V. Wilkov and N. A. Tarasenko, *Chem. Commun.*, 1176 (1969).

[3] B. Beagley, A. G. Robiette, and G. M. Sheldrick, *J. Chem. Soc. A*, 3002 (1968); H. Siebert and J. Eints, *J. Mol. Struct.*, 4, 23 (1969).

[4] As compared to the barriers of comparable phosphines (*e.g.*, methylphenyl-*t*-butylphosphine) which fall in the range of 32–33 kcal/mol[5] at 130°.

[5] R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, 92, 3090 (1970).

[6] The temperature-dependent nmr spectrum of the cyclic tetramer [Me$_2$SiAsMe]$_4$ (E. W. Abel and J. P. Crow, *J. Organometal. Chem.*, 17, 337 (1969)) suggests the possibility that the barrier to inversion at

Evidently, this effect need not be reflected in the ground-state geometry.[3]

The synthesis of **1** was accomplished through phenylsilane reduction of methyl isopropylphenylphosphinate[8] to isopropylphenylphosphine, which was subsequently treated with sodium dispersion in refluxing dioxane followed by trimethylsilyl chloride.[11] Purification of the silylphosphine by fractional distillation (*ca.* 52°, 0.05 mm) afforded a sample of **1** which contained a small amount of unidentified material, as judged by nmr.[12] The nmr spectrum of **1**, together with data for similar phosphines,[13] provides convincing evidence for the assigned structure: δ 7.1–7.7 (m, C_6H_5), 0.10 (d, $^3J_{PH} = 4.0$ Hz, $Si(CH_3)_3$), 2.14–2.83 (m, $CH(CH_3)_2$), 1.20 (dd, $^3J_{PH} = 16.5$ Hz, $^3J_{HH} = 6.9$ Hz, $CH_{3(a)}$), 1.15 (dd, $^3J_{PH} = 14.6$ Hz, $^3J_{HH} = 6.7$ Hz, $CH_{3(b)}$).

As the temperature is increased above 31°, the eight initially well-resolved signals in the isopropyl methyl region coalesce smoothly into four (in the range 55–75°). A line-shape analysis[14] was used to simulate[15] spectra at various rates of exchange. A comparison of these with experimental spectra recorded near coalescence provided a value for the above-cited barrier. Additional evidence that pyramidal inversion at phosphorus is the rate-determining step which corresponds to the measured barrier was provided by a similar nmr analysis of a (crude) sample of **2**, which yielded a barrier of $\Delta G^{\ddagger}_{70} \sim 19.1$ kcal/mol. The fact that the barrier remains essentially unaltered whether the diastereotopic methyl groups are bound to carbon (in **1**) or silicon (in **2**) greatly reduces the remote possibility that a torsional rather than an inversional process is being observed.

The low inversion barriers found in **1** and **2** may be ascribed, in part, to (p–d)π conjugation.[16,18] Such stabilization has been invoked to explain the relatively low barriers to inversion found in diphosphines[20,21] and, possibly, in thiophosphinites.[22] That (p–d)π conjugation may be a dominant effect is suggested by the observation (unpublished work) that the germanium analog of **1** (isopropylphenyltrimethylgermylphosphine) has a pyramidal inversion barrier of $\Delta G^{\ddagger}_{109} = 21.4$ kcal/mol. Since the electronegativity of Ge is closely similar to that of Si,[19] the slightly lower (by 2.5 kcal/mol) barrier of **1** might tentatively be ascribable to more effective (3p–3d)π as compared to (3p–4d)π orbital overlap.

The experimental results justify the expectation[23] that the low electronegativity and the absence of lone pairs on the adjacent silicon atom render this element far more effective than neighboring phosphorus[20] or sulfur[22] in lowering the barrier to pyramidal inversion at phosphorus.

pyramidal arsenic may also be lowered by adjacent silicon. Unfortunately, interpretation of the observed coalescences, which may be due to interconversions of ring conformers, is ambiguous, and no quantitative estimates of barrier heights have been reported.

(7) The only other comparably low barrier to phosphorus inversion previously reported involves a phosphole system ($\Delta G_{25}^{\ddagger} = 16$ kcal/mol) for which aromatic stabilization has been invoked: W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 1442 (1970). It is noteworthy that in this case also the analogous nitrogen compound (pyrrole) is planar: L. Nygaard, J. T. Nielson, J. Kirchheiner, G. Mattesen, J. Rastrup-Anderson, and G. O. Sorensen, *J. Mol. Struct.*, **3**, 491 (1969).

(8) This previously reported[9] phosphinate was here prepared from the corresponding phosphinic acid, itself obtained by Arbuzov rearrangement of diisopropyl phenylphosphonite.[10]

(9) T. H. Siddall, III, and C. A. Prohaska, *J. Amer. Chem. Soc.*, **84**, 2502 (1962).

(10) A. E. Arbuzov, G. Kh. Kamai, and O. N. Belorossova, *J. Gen. Chem. USSR*, **15**, 766 (1945); *Chem. Abstr.*, **41**, 105 (1947).

(11) For the synthesis of related silylphosphines, see W. Kuchen and H. Buchwald, *Chem. Ber.*, **92**, 227 (1959); G. Fritz, *Angew. Chem., Int. Ed. Engl.*, **5**, 53 (1966).

(12) These compounds are extremely sensitive to oxygen (E. W. Abel and I. H. Sabherwal, *J. Chem. Soc. A*, 1105 (1968)) and moisture.

(13) W. McFarlane, *Chem. Commun.*, 229 (1968); G. Märkl and H. Olbrich, *Tetrahedron Lett.*, 3813 (1968).

(14) The line-shape analysis was based on data obtained on a Varian A-60A spectrometer. The sample was a *ca.* 20% v/v solution in C_6D_6 with *ca.* 5% v/v dioxane as internal standard.

(15) G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969).

(16) This conjugation[17] should be enhanced in the transition state for inversion.

(17) E. A. V. Ebsworth, *Chem. Commun.*, 530 (1966).

(18) At present, claims for (p–d)π conjugation in silylphosphines are based predominantly upon chemical evidence such as their very low basicity.[19]

(19) For a thorough discussion of the molecular properties which may be functions of (p–d)π conjugation, see E. A. V. Ebsworth in "Organometallic Compounds of the Group IV Elements," Vol. 1, Part 1, A. G. MacDiarmid, Ed., Marcel Dekker, Inc., New York, N. Y., 1968, Chapter 1.

(20) (a) J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *J. Amer. Chem. Soc.*, 90, 6401 (1968); (b) J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *ibid.*, **92**, 3093 (1970).

(21) The barrier ($E_a = 26$ kcal/mol) in 1,2-dimethyl-1,2-diphenyldiphosphine[20a] reflects a decrease of *ca.* 6 kcal/mol relative to the dialkylarylphosphines.[5]

(22) W. B. Farnham, A. W. Herriott, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 6878 (1969).

(23) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem.*, in press.

Raymond D. Baechler, Kurt Mislow
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received May 2, 1970

Bis(O-fluorosulfato)tetrafluoroxenon(VI) and Bis(O-fluorosulfato)difluoroxenon(IV)

Sir:

The ability of xenon to form compounds with ligands other than fluorine or oxygen has been demonstrated recently for Xe(II).[1–4] There have, however, been no reports of similar compounds for Xe(VI) and Xe(IV).[5] We have prepared $F_4Xe(OSO_2F)_2$ and $F_2Xe(OSO_2F)_2$ from XeF_6 and XeF_4 by reactions with fluorosulfuric acid at −25 to −5°. The reactions occur almost quantitatively when carried out stoichiometrically according to the equations (mmol)

$$XeF_6\ (0.95) + 2HOSO_2F\ (1.87) \longrightarrow F_4Xe(OSO_2F)_2\ (0.93) + 2HF\ (1.8)$$

$$XeF_4\ (0.75) + 2HOSO_2F\ (1.5) \longrightarrow F_2Xe(OSO_2F)_2\ (0.71) + 2HF\ (1.5)$$

Only traces of O_2, $S_2O_5F_2$, and $S_2O_6F_2$ were observed when the HF was removed at −5° after a 1 day reaction time. The progress of the reaction was monitored by observing the disappearance of the solid xenon fluorides in the Kel-F reaction tubes.

The new compounds are yellow-green liquids at 22°. They tend to form glasses at low temperature, but have been observed to crystallize slowly to white solids at −78°. Both compounds are thermally unstable

(1) M. Eisenberg and D. D. DesMarteau, *Inorg. Nucl. Chem. Lett.*, **6**, 29 (1970).

(2) N. Bartlett, M. Wechsberg, F. O. Sladky, P. A. Bulliner, G. R. Jones, and R. D. Burbank, *Chem. Commun.*, 703 (1969).

(3) F. Sladky, *Angew. Chem.*, **81**, 330 (1969).

(4) F. Sladky, *ibid.*, **81**, 536 (1969).

(5) The compound $Xe(O_2CCF_3)_4$ was reported by A. Iskraut, R. Taubenest, and E. Schumacher, *Chimia*, **18**, 188 (1964), but this claim has been disputed: J. G. Malm and E. H. Appelman, *At. Energy Rev.*, **8**, 38 (1969).