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Oxidation of Tris(trifluoromethyl)phosphine

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Oxygen reacts with tris(trifluoromethyl)phosphine by a chain reaction involving the trifluoromethyl radical and its autoxidation. With thermal quenching, tris(trifluoromethyl) phosphate and bis(trifluoromethyl)fluorophosphine oxide are formed. Under conditions of spontaneous ignition the latter compound delivers CF_2, a powerful reducing agent.

Introduction

The chemistry of oxygen is astoundingly diverse in mechanism and kinetics. High versatility is displayed even with the small subset of substrates trivalent phosphorus compounds. Like the lower trialkylphosphines, tris(trifluoromethyl)phosphine, $(CF_3)_3P$, is spontaneously flammable in air.[1] We studied the autoxidation of $(CF_3)_3P$ under a variety of conditions in order to unravel the various reaction paths involved. The thermal decomposition of the (trifluoromethyl)fluorophosphine oxides also proved to be relevant.

Experimental Section

All compounds were handled by vacuum-line methods. Products were fractionated by passing them through cold traps, and each fraction was examined by infrared and sometimes by mass spectroscopy. The analysis of thermal decomposition products was done by NMR and infrared methods. Although no explosions were encountered, shielding should be employed when duplicating the oxidation experiments, particularly if they are to be scaled up.

Starting Material. $(CF_3)_3P$,[1] $(CF_3)_2PF$,[2] CF_3PF_2,[2] and $(CF_3)_3PO$[3] were made by literature methods.

$CF_3P(O)F_2$. The reaction of 3 mmol of CF_3PF_2 with N_2O_4 to give CF_3POF_2 is convenient, but on a 12-mmol scale, the mixture ignited. Boiling point, melting point, NMR, and infrared data agreed with reported values[4] for $CF_3P(O)F_2$ made by partial hydrolysis of CF_3PF_4 (except for a typographical error in the infrared data, giving a peak at 931 cm^{-1} as vs which should be vw).

$(CF_3)_2P(O)F$. This compound is best made by mixing 3 mmol of $(CF_3)_2PF$ with $^1/_2$ atm of air very slowly (to avoid ignition) in a 1 L flask. During 30 min at 25 °C, there was a 5% conversion to $(CF_3)_2P(O)F$, and after 16 h the reaction was essentially complete. A vapor pressure of 760 mm at 5 °C was observed (lit.[5] extrapolated bp 7 °C), and the melting point was −110 °C.

Thermal Decompositions. $(CF_3)_3P$. A 1600-μmol sample of $(CF_3)_3P$ at 1 atm in a sealed glass tube at 320 °C for 16 h was recovered essentially unchanged. A 2% conversion to PF_3 was observed. After 20 h at 360 °C, there was a 30% recovery of $(CF_3)_3P$ and 1100 μmol of PF_3 had formed. After destruction of the PF_3 and SiF_4 in the most volatile fraction with aqueous NaOH, there remained 480 μmol of C_2F_6.

$(CF_3)_3PO$. A 1380-μmol sample of $(CF_3)_3PO$ was maintained at 100 °C in a 1.5-cm^3 glass tube. After 2 h, 10% of the $(CF_3)_3PO$ had decomposed, giving $(CF_3)_3P$, OCF_2, and $(CF_3)_2P(O)F$ as major products. After 6 h, the sample was 50% decomposed and contained $(CF_3)_3PO$, $(CF_3)_3P$, $(CF_3)_2P(O)F$, $(CF_3)_2PF$, $CF_3P(O)F_2$, CF_3PF_2, OPF_3, PF_3, and OCF_2. After 29 h, no starting material remained. The products were (amounts in μmol) 1200 OCF_2, 670 $(CF_3)_3P$, 380 $(CF_3)_2PF$, 134 CF_3PF_2, 110 OPF_3, 90 PF_3, 10 CO, and 10 C_2F_4.

A 2000-μmol sample of $(CF_3)_3PO$ was kept at 25 °C in an NMR tube. After 2 years, the products (in μmol) were 860 $(CF_3)_3PF_2$, 410 CF_3PF_4, 360 $(CF_3)_3P$, 300 $(CF_3)_2PF_3$, 70 PF_5, and an unmeasured amount of CO and COF_2.

When a 1340-μmol sample of $(CF_3)_3PO$ was kept at 130 °C for 20 h in the presence of 10000 μmol of C_2F_4, we obtained the following (in μmol): 1120 $(CF_2)_3$, 714 $(CF_3)_3P$, 312 OPF_3.

$(CF_3)_2P(O)F$. A sample of $(CF_3)_2P(O)F$ (2230 μmol) was kept in a 1.5-cm^3 glass tube at 125 °C for 1 h. The products formed (amounts in μmol) were 1340 OCF_2, 800 $(CF_3)_2PF$, 445 CF_3PF_2, 400 OPF_3, 270 $CF_3P(O)F_2$, 130 $(CF_3)_3PF_2$, and 130 CO.

Another sample of $(CF_3)_2P(O)F$ (2500 μmol) in a 1.5-cm^3 tube after 4 days at 25 °C had changed to the following composition (in μmol): 1070 $(CF_3)_2P(O)F$, 710 $CF_3P(O)F_2$, 710 $(CF_3)_2PF_3$. CO was not measured at this stage. After 10 days at 25 °C, $(CF_3)_2P(O)F$ was absent, and there were 1340 CO, 980 $CF_3P(O)F_2$, 620 $(CF_3)_2PF_3$, 400 CF_3PF_4, 220 CF_3PF_2, 90 $(CF_3)_3PF_2$, 45 OPF_3, and 20 $(CF_3)_2PF$ (in μmol).

$CF_3P(O)F_2$. A sample of $CF_3P(O)F_2$ (2230 μmol) at 100 °C in a 1.5-cm^3 tube was half destroyed in 3.5 h. After 16 h at 100 °C, no starting material remained, and the following products were present (in μmol): 990 OPF_3, 700 OCF_2, 535 CO, 345 PF_3, 345 CF_3PF_2, 345 CF_3PF_4, 140 PF_5, 70 $(CF_3)_3PF_2$, 18 $(CF_3)_2PF_3$.

Oxidation of $(CF_3)_3P$ with Ignition. When oxygen at 0.5 atm pressure was admitted to 535 μmol of $(CF_3)_3P$ in an 80-cm^3 tube at 25 °C, a yellow flame front passed through the gas. The volatile condensable products were as follows (in μmol): 760 OCF_2, 225 OPF_3, 180 CF_4, 90 C_2F_6, 45 $(CF_3O)_3PO$, 40 CO_2, 20 PF_3.

In another experiment, $(CF_3)_3P$ (893 μmol) was condensed at −196 °C into an 80-cm^3 glass seal-off tube. Then O_2 (6700 μmol) was admitted and the tube sealed. The tube was allowed to warm in air, and after considerable time (probably the tube was near room temperature), the gas ignited and burned slowly. The condensable (at −196 °C) products were found to be as follows (in μmol): 582 OCF_2, 246 OPF_3, 134 CF_4, 112 $(CF_3O)_3PO$, 90 C_2F_6, 90 PF_3, 50 CO_2. A trace of hydrolyzable, nonvolatile oil on the reaction walls was titrated and found to have a pK_1 of 1.1 and a pK_2 of 4.0, corresponding to values for $CF_3P(O)(OH)_2$.[6]

Inhibition of Reaction with Oxygen. When the two experiments described above were repeated, but 50 μmol of toluene was present, there was no ignition, and $(CF_3)_3P$ was recovered unchanged. A sample of 50 μmol of $(CF_3)_3P$ was mixed with 5 μmol of toluene and 1200 μmol of O_2 (0.5 atm) in a 50-cm^3 infrared gas cell. No change was observed in 7 days.

Reaction of $(CF_3)_3P$ with Oxygen without Ignition. A 1200-μmol sample of $(CF_3)_3P$ was condensed (−196 °C) into the test tube end attached to a 1-L flask. Next, 7320 μmol of O_2 was admitted and the flask closed off. The test tube end was maintained at −78 °C (the vapor pressure of $(CF_3)_3P$ is 4 mm at −78 °C) for 1 h while the main body of the flask was at 25 °C. The liquid $(CF_3)_3P$ was allowed to warm to room temperature over a period of 2 h by warming the cooling bath around the test tube end. No ignition was observed. The condensable contents of the flask were as follows (in μmol): 670 $(CF_3O)_3PO$, 490 OCF_2, 400 $(CF_3)_2P(O)F$.

A similar experiment employed 1650 μmol of $(CF_3)_3P$ and 6500 μmol of O_2 in a sealed 80-cm^3 tube. The liquid $(CF_3)_3P$ was maintained at −78 °C for 36 h, while the upper part of the tube was at 25 °C. The products were as follows (in μmol): 1250 OCF_2, 1180 $(CF_3)_2P(O)F$, 360 $(CF_3O)_3PO$.

A 500-cm^3 flask was packed with 70 g of stainless steel ribbon ("Miracle Scour Power") to serve as a heat sink. $(CF_3)_3P$ (1400 μmol) was brought into the flask and allowed to warm to 25 °C. Then 20000 μmol of O_2 was admitted. After 1 h the products were fractionated and found to be as follows (in μmol): 1200 $(CF_3O)_3PO$, 400 COF_2, 100 $(CF_3)_2P(O)F$.

Characterization of $(CF_3O)_3PO$. The vapor pressure of $(CF_3O)_3PO$ conforms to the equation $\log p = 7.330 - 1445/T$. The extrapolated boiling point is 52 °C and the melting point is −86 °C. The gas density as measured corresponds to $M_r = 302$. The mass spectrum has a parent peak at 301.9409, calcd 301.9391. Negative ion mass spectroscopy gives a prominent OCF_3^- peak. ^{19}F NMR shows a doublet centered at 55.6 ppm from $FCCl_3$, and $J_{P-F} = 6$ Hz. Strong infrared absorption is observed at 1390, 1380, 1280, 1260, 1250, 1163, 1036, and 815 cm^{-1}.

A 1500-μmol sample of $(CF_3O)_3PO$ at 60 °C for 3 days gave 4500 μmol of OCF_2 and 1500 μmol of OPF_3. $(CF_3O)_3PO$ is destroyed with water or aqueous KOH without formation of any CF_3H.

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Autoxidation of Trifluoromethyl Radicals. Photochemical irradiation of hexafluoroacetone and oxygen in a Pyrex container produced an appreciable amount of SiF_4 and COF_2. A photochemical reactor was constructed from a 500-cm^3 resin kettle coated on the inside with Teflon and fitted with a quartz immersion lamp having an output of 2.5 W at 2537 Å. A mixture of 7100 μmol of hexafluoroacetone and 11 500 μmol of O_2 was irradiated for 15 h at 40 °C. Vacuum-line fractionation, confirmed by infrared and NMR spectra,[7,8] gave 1800 μmol of CF_3OOCF_3, 600 μmol of CF_3OOOCF_3, and a recovery of 4400 μmol of $(CF_3)_2CO$. A comparable result was obtained by irradiation at −20 °C.

Discussion

Thermally Quenched Oxidation. The inhibition of the reaction of oxygen with $(CF_3)_3P$ in the presence of radical traps suggests that the autoxidation is a radical chain process like that of the hydrocarbon phosphines.[9] In the absence of radical traps, but with thermal quenching, high yields of the new compound tris(trifluoromethyl) phosphate are obtained. Displacement of CF_3 radicals from $(CF_3)_3P$ with *tert*-butoxy radicals has been unambiguously demonstrated.[10] By analogy, the following chain process is suggested:

$$(CF_3)_3P + CF_3OO\cdot \rightarrow CF_3OOP(CF_3)_2 + CF_3\cdot \quad (1)$$

$$CF_3OOP(CF_3)_2 + CF_3OO\cdot \rightarrow (CF_3OO)_2PCF_3 + CF_3\cdot \quad (2)$$

$$CF_3\cdot + O_2 \rightarrow CF_3OO\cdot \quad (3)$$

$$(CF_3OO)_2PCF_3 \rightarrow (CF_3O)_3PO \quad (4)$$

That CF_3 reacts easily with O_2 to give $CF_3OO\cdot$ is reasonably certain,[11,12] and the formation of CF_3OOCF_3 and CF_3OOOCF_3 from CF_3 and O_2 lends support to this idea. The following series of reactions might account for the formation of these products:

$$CF_3\cdot + O_2 \rightarrow CF_3O_2\cdot \quad (3)$$

$$2CF_3O_2\cdot \rightleftarrows CF_3OOOOCF_3 \quad (5)$$

$$CF_3OOOOCF_3 \rightleftarrows CF_3O\cdot + CF_3OOO\cdot \quad (6)$$

$$CF_3OOO\cdot \rightleftarrows CF_3O\cdot + O_2 \quad (7)$$

$$2CF_3O\cdot \rightarrow CF_3OOCF_3 \quad (8)$$

$$CF_3O\cdot + CF_3OO\cdot \rightarrow CF_3OOOCF_3 \quad (9)$$

The reverse reactions of (7)[13] and (9)[14,15] have been demonstrated. There has been a previous report on the formation of bis(trifluoromethyl) trioxide from the trifluoromethyl radical and oxygen.[16]

Initiation Step. Tris(trifluoromethyl)phosphine does not react with oxygen much below room temperature although the CF_3 radical displacement proceeds well at much lower temperatures. The high activation energy initiation step is tentatively ascribed to

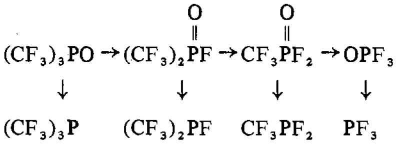
$$(CF_3)_3P + O_2 \rightarrow (CF_3)_3PO_2 \quad (10)$$

$$(CF_3)_3PO_2 \rightarrow 2CF_3\cdot + CF_3PO_2 \quad (11)^{17}$$

A trace of an oily, hydrolyzable product corresponding to $(CF_3PO_2)_n$ was found on the wall of the reaction flask after oxidation of $(CF_3)_3P$. C_2F_6 was also consistently observed as a minor product, but attempts to optimize CF_3PO_2 formation or isolate $(CF_3)_3PO_2$ by suppressing the subsequent chain reaction were not successful.

Combustion of $(CF_3)_3P$. The other minor products, CF_4, PF_3, PF_5, CO, CO_2, and occasionally C_2F_4, observed in the oxidation of $(CF_3)_3P$ with spontaneous ignition implicate chemistry beyond thermal decomposition of $(CF_3O)_3PO$, which cleanly gives $3COF_2$ and OPF_3. The isolation of bis(trifluoromethyl)fluorophosphine oxide, $(CF_3)_2P(O)F$, from the thermally quenched reaction is the clue to these products. $(CF_3)_2P(O)F$ presumably arises from $CF_3OOP(CF_3)_2$ formed in reaction 1 by elision of OCF_2 and a fluorine shift from C to P. Since a fluorine shift from C to P is a common occurrence for pentavalent phosphorus, it is likely that the initially formed (trifluoromethylperoxy)bis(trifluoromethyl)phosphine rearranged to (trifluoromethoxy)bis(trifluoromethyl)phosphine oxide.[18]

The (trifluoromethyl)phosphine oxides, like the (trifluoromethyl)fluorophosphoranes,[19] undergo CF_2 elision under mild conditions (horizontal sequence (12)).



$$\begin{tikzcd} (CF_3)_3PO \arrow[r] \arrow[d] & (CF_3)_2\overset{\overset{O}{\|}}{P}F \arrow[r] \arrow[d] & CF_3\overset{\overset{O}{\|}}{P}F_2 \arrow[r] \arrow[d] & OPF_3 \arrow[d] \\ (CF_3)_3P & (CF_3)_2PF & CF_3PF_2 & PF_3 \end{tikzcd} \quad (12)$$

This process is complicated by the oxygen-abstracting proclivity of CF_2,[20] which reduces the phosphine oxides to the phosphines. This has been demonstrated by heating $(CF_3)_3PO$ at 100 °C and observing each of the products in eq 12. Yet further complexity arises in the presence of oxygen, which reoxidizes $(CF_3)_2PF$ and CF_3PF_2 to the corresponding phosphine oxides. In addition, CF_2 can fluorinate[20] the phosphine oxides.

$$CF_2 + (CF_3)_nP(O)F_{3-n} \rightarrow CO + (CF_3)_nPF_{5-n}$$
$$n = 0\text{–}3$$

This CO may give rise to the small amount of CO_2 observed.[15,21] Paradoxically, the oxidation of $(CF_3)_3P$ generates the powerful reducing agent CF_2, which accounts for the production of PF_3 and CO.

Carbon tetrafluoride is observed as an oxidation product of tris(trifluoromethyl)phosphine only when the latter ignites. Its genesis is not clear; it may arise from decomposition of fluorocarbon oxides to give strong fluorinating agents.

$$CF_3OO\cdot \rightarrow CF_2O + \cdot OF \quad (13)^{11}$$

$$CF_3O\cdot \rightarrow CF_2O + F\cdot \quad (14)^{22}$$

$$CF_3OOCF_3 \rightarrow CF_2O + CF_3OF \quad (15)^{23,24}$$

$$CF_3OF \rightarrow CF_2O + F_2 \quad (16)^{23}$$

These may react with the CF_3 radicals or more directly with tris(trifluoromethyl)phosphine.[25] Difluorocarbene is known to react with fluorinating agents to give CF_4,[19] and it is possible that the CF_2 flux is high enough during combustion to be significant. Tetrafluoromethane formation from "hot" trifluoromethyl[11] radicals may also be involved here.

The high thermal stability of $(CF_3)_3P$ makes it unlikely that it contributes to the combustion products without interaction with oxygen. Similarly, $(CF_3)_2PF$ and CF_3PF_2 are essentially unchanged after 24 h at 300 °C. A literature report[26] claiming that CF_3PF_2 disproportionates to CF_3PF_4 and $(CF_3P)_x$ at 115 °C is in error.[27]

Although most phosphines give substantial amounts of the phosphine oxide on oxidation,[9] this is not the case with tris(trifluoromethyl)phosphine, since elimination of $CF_3\cdot$ bound to P from $CF_3O\dot{O}\dot{P}(CF_3)_3$ (reaction 1) is much preferred over loss of $CF_3O\cdot$. However, $(CF_3)_2PF$, CF_3PF_2, and PF_3 behave like the trialkyl- and arylphosphines in favoring β cleavage, $RO\dot{O}\dot{P}R'_3 \rightarrow RO\cdot + OPR'_3$.

Another possible pathway to phosphine oxide formation is the reduction of the initially formed dioxygen adduct, R_3PO_2, with R_3P. In order to test this possibility with $(CF_3)_3P$, a large excess of PF_3[28] was introduced before oxygen was admitted at 25 °C. Tris(trifluoromethyl)phosphine oxide was not observed; the PF_3 was converted to OPF_3 and nearly all $(CF_3)_3P$ was recovered unchanged. This can be attributed to the generation of some trifluoromethyl radicals by reactions 10 and 11 followed by transfer of peroxy atoms to PF_3 and reoxidation of trifluoromethoxy radicals in a catalytic cycle.

$$CF_3\cdot + O_2 \rightarrow CF_3OO\cdot \quad (3)$$

$$CF_3OO\cdot + PF_3 \rightarrow CF_3O\cdot + OPF_3 \qquad (17)$$

$$CF_3O\cdot + O_2 \rightarrow CF_3OOO\cdot \qquad (7)$$

$$CF_3OOO\cdot + PF_3 \rightarrow CF_3OO\cdot + OPF_3 \qquad (18)$$

Registry No. $(CF_3)_3P$, 432-04-2; $(CF_3)_3PO$, 423-01-8; $(CF_3)_2P(O)F$, 34005-83-9; $CF_3P(O)F_2$, 19162-94-8; CF_3PF_2, 1112-04-5; $(CF_3)_2PF$, 1426-40-0; $(CF_3O)_3PO$, 68423-90-5.

References and Notes

(1) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).
(2) A. B. Burg and G. Brendel, *J. Am. Chem. Soc.*, **80**, 3198 (1958).
(3) A. B. Burg and A. J. Sarkis, *J. Am. Chem. Soc.*, **87**, 238 (1965).
(4) J. E. Griffiths, *Spectrochim. Acta, Part A*, **24**, 115 (1968).
(5) R. C. Dobbie, *J. Chem. Soc. A*, 2894 (1971).
(6) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 3598 (1954).
(7) L. R. Anderson and W. B. Fox, *J. Am. Chem. Soc.*, **89**, 4313 (1967).
(8) P. G. Thompson, *J. Am. Chem. Soc.*, **89**, 4316 (1967).
(9) C. Walling and M. S. Pearson, *Top. Phosphorus Chem.*, **3**, 1 (1966).
(10) P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 6033 (1972).
(11) I. McAlpine and H. Sutcliffe, *J. Phys. Chem.*, **73**, 3215 (1969).
(12) J. Maruani, C. A. McDowell, H. Nakajima, and P. Raghunathan, *Mol. Phys.*, **14**, 349 (1968).
(13) R. W. Fessenden, *J. Chem. Phys.*, **48**, 3725 (1968).
(14) S. W. Benson and R. Shaw, "Organic Peroxides", D. F. Swern, Ed., Wiley, New York, 1970, p 124.
(15) F. A. Hohorst, D. D. Des Marteau, L. R. Anderson, D. E. Gould, and W. B. Fox, *J. Am. Chem. Soc.*, **95**, 3866 (1973).
(16) V. A. Ginsburg et al., *Dokl. Akad. Nauk SSSR*, **149**, 97 (1963).
(17) A possibly analogous fragmentation has been observed in the reaction of bis(trifluoromethyl)carbene with oxygen: $(CF_3)_2CO_2 \rightarrow 2CF_3\cdot + CO_2$ (W. Mahler, unpublished work).
(18) A similar rearrangement was suggested for the formation of $CF_3OP(O)F_2$: P. A. Bernstein and D. D. Des Marteau, *J. Fluorine Chem.*, **2**, 315 (1972).
(19) W. Mahler, *Inorg. Chem.*, **2**, 230 (1963).
(20) W. Mahler, *J. Am. Chem. Soc.*, **90**, 523 (1968).
(21) We observed the oxidation of CO to CO_2 with O_2 at 25 °C catalyzed by $(CF_3)_3P$ but found it not reproducible. Presumably, the reaction is analogous to the CF_3-catalyzed oxidation of PF_3 (vide infra) but more easily subject to inhibition.
(22) R. C. Kennedy and J. B. Levy, *J. Phys. Chem.*, **76**, 3480 (1972).
(23) R. S. Porter and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 5628 (1957).
(24) J. B. Levy and R. C. Kennedy, *J. Am. Chem. Soc.*, **94**, 3302 (1972).
(25) $(CF_3)_3P$ reacts with SbF_5 to give CF_4.
(26) H. G. Ang and R. Schmutzler, *J. Chem. Soc. A*, 702 (1969).
(27) The observed $(CF_3P)_x$ arises from the reducing action of SbF_3, $CF_3PI_2 + SbF_3 \rightarrow I_2SbF_3 + (CF_3P)_x$, and the I_2SbF_3 oxidizes some of the CF_3PF_2. In fact, we had found that $CF_3PF_2 + I_2 + SbF_3$ is a good synthesis method for CF_3PF_4.
(28) A mixture of PF_3 and O_2 does not react below 500 °C and requires no less than the oxygen–hydrogen flame or electric spark for ignition.[29]
(29) H. Moissan, *C. R. Hebd, Seances Acad. Sci.*, **102**, 1245 (1886).

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Trimethylamine, Trisilylamine, and Trigermylamine: A Comparative Study of Ionization Energies, Charge Distribution, and Bonding

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Calculations of the electronic structures of $(CH_3)_3N$, $(SiH_3)_3N$, and $(GeH_3)_3N$ by the Xα scattered-wave self-consistent-field method give a good account of the measured ionization energies and allow a detailed assessment of the various bond types. Interactions involving d orbitals are most important in the silicon compound, in which the highest occupied ("lone pair") orbital is stabilized most; significant pπ–pπ bonding is found in deeper orbitals. Other features of the bonding are the appreciable interaction between nitrogen and the M–H bonds and the high polarities of the M–H and M–N bonds. The planarity of $(SiH_3)_3N$ is ascribed principally to electrostatic rather than to d-orbital interactions.

Introduction

The substitution of a silyl group for a methyl group has well-defined effects on the properties of a neighboring oxygen or nitrogen atom; the ionization energy is increased, donor properties are weakened, and the interbond angle is increased. The planarity of the skeletal conformations of trisilylamine[1] and trigermylamine,[2] as contrasted with the pyramidal structures of trimethylamine,[3] trisilylphosphine,[4] and trisilylarsine,[5] has frequently been attributed to pπ–dπ bonding, especially in trisilylamine. Such interactions provide at least a plausible explanation for the other properties of the Si–N and Si–O bonds and account for some features of the photoelectron spectra of halosilanes.[6] The evidence for π bonding has been critically reviewed[7] for many types of silicon compounds.

While there seems no doubt that pπ–dπ interactions occur in trisilylamine, they are not the only important factor,[8] and may not, in themselves, induce planarity. A theoretical investigation[9] of the (hypothetical) molecule SiH_3NH_2 confirms the occurrence of weak pπ–dπ conjugation in the highest (N lone pair) molecular orbital, but it has only a small effect on the difference in energy between the planar and pyramidal forms, the latter being favored slightly, as found experimentally for *N*-silyldimethylamine.[10] The tendency toward planarity in related compounds is ascribed principally to electrostatic repulsion arising from inductive release from silicon to nitrogen[9] and also to nonbonded interactions.[11] The inversion barrier at three-coordinated nitrogen in fact depends on many factors,[12] and all pairwise interactions contribute significantly,[13] though their relative importance varies. It is therefore important to carry out accurate calculations on certain key molecules, especially those whose properties are known in detail.

Few such investigations have been reported. The bond energies in Me_3NH^+ and $Me_3N\cdot BH_3$ have been calculated in a Hartree–Fock framework with a 4-31G basis set,[14] but it is difficult to extend calculations of this type to molecules with several heavy atoms, particularly when d orbitals are included. The orbital ordering and symmetry species of the methyl amines have been studied by CNDO/2 and MINDO/2 methods,[15] principally in relation to their photoelectron spectra, and, in another (exploratory) calculation,[16] orbital compositions and ionization energies of the N lone-pair orbitals were obtained for two conformations of $(CH_3)_3N$ and $(SiH_3)_3N$. In view of the results referred to above, it is important to determine the lower levels also and to carry the comparison as far as $(GeH_3)_3N$. We have therefore made a comparative study of the electronic structures of the three molecules $(CH_3)_3N$, $(SiH_3)_3N$, and $(GeH_3)_3N$. We have used the Xα method to obtain good accuracy (as judged by a comparison of calculated and experimentally determined ionization energies) with reasonable economy in computer time. The results are used to assess the chemical bonding in these molecules.

Calculation Procedure

The calculations were made by the overlapping-spheres version of the all-electron self-consistent-field Xα scattered-wave method[17]

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