The mechanism suggested above also explains in part the effect of pH on the specific rate of disappearance of Cu(III) in the absence of added OH scavengers. The most probable mechanism in acid solutions is

$$\mathrm{OH} + \mathrm{Cu(III)} \longrightarrow \mathrm{Cu^{2+}} + \mathrm{H_2O_2} \qquad (12)$$

$$\mathrm{OH} + \mathrm{OH} \longrightarrow \mathrm{H_2O_2} \qquad (13)$$

These reactions are much faster than reaction 4. These reactions suggest that the decay of Cu(III) in the absence of OH scavengers should be a second-order process. However, the decay plots suggest a first-order decay process (though the calculated rates depend on the dose delivered). These facts might be explained in part by the fact that the yield of Cu^+ increases and the yield of Cu(III) decreases with decreasing pH due to the competition between the reactions $e_{aq}^- + H_3O^+ \rightarrow$ H and $e_{aq}^- + N_2O \rightarrow N_2 + OH$. Thus at pH 3 and 5×10^{-4} M Cu^{2+} the calculated yields are $G(Cu^+) = 1.5$ and $G(Cu(III)) = 4.5$. The increased rate of the disappearance of Cu(III) and the fact that it approaches a first-order mechanism cannot be due only to the increase in $G(Cu^+)$ because $G(Cu(III)) > G(Cu^+)$. It seems that the solutions contained a very small concentration, about 1×10^{-6} M, of an impurity which is a good OH radical scavenger. This impurity was probably introduced with the N_2O and might be NO or NO_2. Alternatively the possibility exists that OH radicals do react with N_2O with a specific rate of about 10^5 M^{-1} sec^{-1}. That the OH scavanger was introduced with the N_2O was checked by diluting the N_2O with Ar. The results indicated a somewhat slower decay of Cu(III) as expected. However, their quantitative analysis is difficult due to the accompanied increase in the yield of Cu^+. The suggested effect of pH and Cu^{2+} concentration on the concentration of $CuOH^{2+}$, Cu^{3+}, and OH explains also their effect on the initial absorption after the pulse. The value of K_2 was not calculated because at least two equilibria are involved and the limit of accuracy of the results was ±15%. The shift of the maximum of the absorption band to the uv with decreasing pH seems to be mainly due to the larger contribution of OH radicals to the absorption, having a maximum at 230 nm,[10] though also a difference in absorbance between Cu^{3+}(aq), $CuOH^{2+}$(aq), and $Cu(OH)_2^+$(aq) is expected.[2] (The maximum of absorption of CuO_2^- is in the range of 400 nm.[11])

The mechanism suggested for the decomposition of Cu(III) in aqueous solutions explains in part the role of Cu^{2+} as a catalyst in several redox reactions where Cu(III) has been suggested to be an intermediate.[12] Cu(III) can be formed by different oxidants in the presence of ligands which lower the redox potential of the couple Cu(III)–Cu^{2+}. The trivalent copper ions seem to oxidize slowly, if at all, reductants which are not ligands in the inner sphere of the copper ions. However the Cu(III) ions form OH radicals in a low concentration for a relatively long time due to equilibrium 1. It is suggested that these OH radicals are the oxidizing agents in part of the catalytic reactions involving trivalent copper.

Acknowledgments.—The author is indebted to Dr. M. S. Matheson for his encouragement and discussions throughout this work. He also wishes to thank Mr. W. A. Mulac and Miss C. Goldenberg for their invaluable assistance in all phases of these experiments and Mr. J. Ogdan and the Linac group at Argonne for their careful operation of the linear accelerators.

[10] P. Pasberg, H. Christensen, J. Rabani, G. Nilsson, J. Fenger, and S. O. Nielsen, *J. Phys. Chem.*, **73**, 1029 (1969).

[11] I. Pecht, Ph.D. Thesis, The Weizmann Institute of Science, Rehovoth, Israel, 1967.

[12] For a general discussion see M. Anbar, *Advan. Chem. Ser.*, **No. 49**, 126 (1965).

Notes

CONTRIBUTION FROM THE MIDWEST RESEARCH INSTITUTE,
KANSAS CITY, MISSOURI 61110

Solid–Solid Phase Transitions Determined by Differential Scanning Calorimetry. III. Organosilicon Compounds

BY E. MURRILL AND L. W. BREED*

Received March 30, 1970

When Gilman first reported the synthesis of tetrakis(trimethylsilyl)silane, he commented on its unusually high melting point (261–263°) in comparison with that of the linear dodecamethylpentasilane, which is a liquid at room temperature.[1] We have found that tetrakis(trimethylsilyl)silane undergoes a solid-state transition at −32 to −35° to a plastic crystalline mesophase, a temperature that does not differ greatly from the reported melting point of dodecamethylpentasilane, −34°.[2] The analogy of this system with the *n*-pentane–neopentane system is obvious. Although *n*-pentane melts at −129.7°, neopentane must be heated to −16.5° for fusion but has a solid-state transition at −133°.[3] On thermal analysis, tetrakis(trimethylsilyl)silane sublimes at 282–285°, which is close to the value for the boiling point of dodecamethylpentasilane that can be obtained by extrapolating its reported boiling point, 135–136° (13 mm). The mesocrystalline phase of tetrakis(trimethylsilyl)silane is stable to such a high temperature that it has virtually no liquid range.

[1] H. Gilman and C. L. Smith, *J. Amer. Chem. Soc.*, **86**, 1454 (1964).

[2] M. Kumada and M. Ishidawa, *J. Organometal. Chem.*, **1**, 153 (1963).

[3] I. Nitta, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **112**, 234 (1959).

TABLE I

TRANSITION AND FUSION TEMPERATURE FOR TRISILYLAMINE DERIVATIVES

Structure	Lit. temp, °C		Exptl temp, °C	
	Transition	Fusion	Transition	Fusion
$N(Si(CH_3)_3)_3$	-41^a	$70–71^b$	-29	62–66
$(CH_3)_3SiN(Si(CH_3)_2Cl)_2$			3	68–76
$(CH_3)_3SiN(Si(CH_3)_2N(CH_3)_2)_2$			-8 to -10	77–85
$N(Si(CH_3)_2Cl)_3$		$73–75^c$	14	80–91
$((CH_3)_3Si)_2NSi(CH_3)_2Cl$	-25^a	$58–60^d$		
$((CH_3)_3Si)_2NSi(CH_3)Cl_2$	-31^a	$80–85^e$		
$((CH_3)_3Si)_2NSiCl_3$	-36^a	$80–85^d$		

[a] Reference 7. [b] J. Goubeau and J. Jimenez-Barbera, *Z. Anorg. Allg. Chem.*, **303,** 15 (1960). [c] U. Wannagat and E. Bogusch, *Inorg. Nucl. Chem. Lett.*, **2,** 97 (1966). [d] U. Wannagat and H. Niederpruem, *Z. Anorg. Allg. Chem.*, **308,** 337 (1964). [e] U. Wannagat and H. Buerger, *ibid.*, **326,** 310 (1964).

Many plastic crystals, for example 2,2,3,3-tetramethylbutane, which has a liquid range of about 4°, exhibit this phenomenon.

Timmermans first recognized that many polymorphic compounds which have a high degree of molecular symmetry have very small entropies of fusion, the value being of the order of the communal entropy. More recent studies of these molecular crystals, which he called plastic crystals, have shown that only the centers of gravity of the molecules acquire freedom on melting and that molecular reorientational freedom about the center of gravity occurs in a transition at some lower temperature.[4] As a consequence much greater gains in entropy are observed at the transitions and the solid mesophase can therefore be considered to be energetically much closer to a liquid than a solid. The plastic crystalline phase (isotropic solid) is sometimes confused with the liquid crystalline phase (anisotropic liquid) in which full molecular reorientational freedom is not gained at the fusion temperature.

A number of other organosilicon-containing substances also have plastic crystalline phases. Hexamethyldisilane has a transition at $-51.4°$ (ΔS = 10.5 eu) and a fusion temperature of 14.5° (ΔS = 2.51 eu).[5] Some time ago, we observed that such transitions could be found in certain trisilylamine derivatives.[6] Recently reported nmr studies have confirmed that other trisilylamine derivatives, $[(CH_3)_3Si]_2NSi(CH_3)_nCl_{3-n}$ (n = 0–3), have "liquid-like" solid phases.[7] A summary of transition and fusion temperatures for trisilylamines obtained in this laboratory and reported in the literature is presented in Table I.

The fusion temperatures recorded by differential thermal analysis are rather broad. The broadness can be explained in part by instrumental factors but can also be attributed to the low heats of fusion, since freezing points are depressed and broadened to a much greater degree by impurities in substances with small heats of fusion (as in molecular weight determinations with camphor, also a plastic crystal). The transition temperatures, which represent a change that is energetically much closer to the usual fusion phenomenon, were sharp and would have been entirely satisfactory as a measure of purity as a melting point for an organic substance. All the samples used in this work were of sufficient purity to give satisfactory elemental, infrared, and nmr analyses. The elemental analyses for $N(Si(CH_3)_2Cl)_3$, which we have not reported before but which Wannagat has previously reported with a considerably different melting point, are included in the Experimental Section. Analytical data for the other compounds are reported in our earlier publication.[6]

The occurrence of the mesocrystalline phase is extremely sensitive to changes in molecular geometry. For example, the following trisilylamines have normal melting points and do not exhibit a mesocrystalline phase: $(CH_3)_3SiN(Si(CH_3)_2H)_2$, $-48°$; $(CH_3)_3SiN(Si(CH_3)_2OCH_3)_2$, $-55°$; $N(Si(CH_3)_2OCH_3)_3$, $-18°$. The requirement that tris(trimethylsilyl)amine as an isotropic solid be nearly symmetrical in three dimensions does not seem to be entirely consistent with the often invoked planarity or near planarity of the Si_3N structure in methyl-substituted trisilylamines. The assumption of near planarity is usually based on Goubeau's measurement of a dipole moment of 0.51 D for tris(trimethylsilyl)amine[8] and by analogy of the coplanarity of the Si_3N structures in trisilylamine and *N,N'*-bis(trimethylsilyl)tetramethylcyclodisilazane, which have been established by X-ray diffraction measurements.[9] Coplanarity is also frequently considered as coincidental with π bonding in the Si_3N structure although it has recently been pointed out that substantial π bonding is possible in nonlinear and pyramidal systems.[10]

Enthalpies and entropies of transition and fusion determined by differential thermal calorimetry are reported in Table II. Even within the limitations of the method, the low heat of fusion of tris(trimethylsilyl)amine is consistent with the simple acquisition of communal entropy at the melting point. Since conformational as well as reorientational freedom may be acquired at the transition temperatures, the entropy values for tris(trimethylsilyl)amine and tetrakis(tri-

---

(4) For reviews on plastic crystals see L. A. K. Staveley, *Ann. Rev. Phys. Chem.*, **13,** 351 (1962); J. Timmermans, *J. Phys. Chem. Solids*, **18,** 1 (1961); J. G. Aston in "Physics and Chemistry of the Organic Solid State," Vol. I, D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience, London, 1963, Chapter 9.

(5) H. Suga and S. Seki, *Bull. Chem. Soc. Jap.*, **32,** 1088 (1959); *Chem. Abstr.*, **54,** 14902 (1960).

(6) L. W. Breed and R. L. Elliott, *J. Organometal. Chem.*, **11,** 447 (1968).

(7) H. Levy, II, *J. Inorg. Nucl. Chem.*, **29,** 1859 (1967).

(8) J. Goubeau and J. Jimenez-Barbera, *Z. Anorg. Allg. Chem.*, **303,** 15 (1960).

(9) K. Hedeberg, *J. Amer. Chem. Soc.*, **77,** 6491 (1955); P. J. Wheatley, *J. Chem. Soc.*, 1721 (1962).

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

TABLE II

ENTHALPIES AND ENTROPIES OF TRANSITION AND FUSION FOR SEVERAL ORGANOSILICON COMPOUNDS

	Transition		Fusion	
	ΔH, cal/g	ΔS, eu	ΔH, cal/g	ΔS, eu
Tetrakis(trimethylsilyl)-silane	8.62	11.5	...	...
Tris(trimethylsilyl)amine	8.08	7.7	1.81	1.3
N,N'-Bis(trimethylsilyl)-tetramethylcyclodisil-azane	...	...	18.93	17.6
Hexamethylcyclotrisiloxane	...	...	21.59	14.4

methylsilyl)silane indicate that not much greater overall conformational freedom is acquired than in the transition for hexamethyldisilane (10.5 eu). For comparison, thermal data for the fusion of two substances not exhibiting a mesocrystalline phase are also reported.

Experimental Section

All qualitative data were determined with a Du Pont differential thermal analyzer at a heating rate of 15°/min in an air atmosphere. The quantitative data were obtained with the differential scanning calorimeter module at a heating rate of 10°/min. The procedure and calibration were described earlier.[11] Tetrakis(trimethylsilyl)silane was prepared by Gilman's procedure[1] and tris(trimethylsilyl)amine by Lehn's procedure.[12] The synthesis of *N,N'*-bis(trimethylsilyl)tetramethylcyclodisilazane[13] as well as bis(chlorodimethylsilyl)trimethylsilylamine and bis(dimethylamino)dimethylsilylamine[6] has been described elsewhere. Tris(chlorodimethylsilyl)amine was prepared by Wannagat's procedure[14] and had the following elemental analyses. *Anal.* Calcd for $C_6H_{18}Cl_3NSi_3$: C, 24.44; H, 6.15; Cl, 36.08; N, 4.75; Si, 28.58. Found: C, 24.62; H, 6.31; Cl, 36.10; N, 4.81; Si, 28.30.

Acknowledgments.—This research was supported by the National Aeronautics and Space Administration under Contract NAS8-21452 and monitored by the Space Science Laboratory.

[11] E. Murrill and L. W. Breed, *Thermochim. Acta*, in press.

[12] W. L. Lehn, *J. Amer. Chem. Soc.*, **86**, 305 (1964).

[13] L. W. Breed, W. L. Budde, and R. L. Elliott, *J. Organometal. Chem.*, **6**, 676 (1966).

[14] U. Wannagat and E. Bogusch, *Inorg. Nucl. Chem. Lett.*, **2**, 97 (1966).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08540

Raman Intensities and Bond Orders in the Hexacarbonyls of Chromium, Molybdenum, and Tungsten[1]

BY ARISTIDES TERZIS AND THOMAS G. SPIRO*

Received June 4, 1970

Few questions have interested inorganic chemists more than the extent of π back-bonding from metal to ligand in the transition metal carbonyls and their derivatives. As the most symmetric representatives of this class of molecules, the group IV hexacarbonyls have attracted particular attention. Recently Jones, *et al.*,[2] carried out a very thorough analysis of the vibrational spectra of these molecules, including $^{12}C^{18}O$ and $^{13}C^{16}O$ isotopes, and determined accurate force constants. The order of the primary metal–carbon stretching constants and by implication that of the M–C bond strengths is W > Cr $\gtrsim$ Mo. This order is reproduced in estimates of M–C bond energies from kinetic[3] and photoionization[4] data. It has been suggested[4] that the origin for this order lies in an irregular variation of valence orbital ionization potentials for the metal atoms. Molecular orbital calculations support the impression of extensive donation of metal electrons to the π^* carbonyl orbitals.[5–7]

Absolute Raman intensities offer the promise of an independent estimate of π bonding. From the intensities of totally symmetric modes one can obtain bond polarizability derivatives by a well-defined transformation.[8] It has long been recognized that these derivatives are related to covalency, and they have been interpreted as reflecting the extent of π bonding in various molecules.[9,10] Recently Long and Plane proposed an equation that relates bond polarizability derivatives directly to bond order.[11] While the theoretical basis for the equation is very approximate, it has proved quite successful in predicting polarizability derivatives for a variety of well-characterized molecules.

The group VI hexacarbonyls provide a particularly opportune subject for a Raman intensity study. Because of their high symmetry, the only internal coordinates that contribute to totally symmetric modes are the two of interest here: M–C and C–O stretching. The problem of coordinate mixing is therefore reduced to a minimum. Furthermore the degree of mixing for the two coordinates can be evaluated with considerable confidence, thanks to the accurate force constants calculated by Jones, *et al.*[2]

Experimental Section

The laser Raman spectrometer and its intensity calibration have been described elsewhere.[12] The 6471-Å line of the Ar–Kr laser was used for excitation. The hexacarbonyls were obtained from Alfa Inorganics. Raman intensities for the A_{1g} modes were measured in CCl_4 solution for $Cr(CO)_6$ and $Mo(CO)_6$ and in CS_2 solution for $W(CO)_6$. Concentrations ranged from 0.01 to 0.07 *M*. The intensities were corrected for instrument response and converted to normal mode polarizability derivatives, $\bar{\alpha}'_Q$, with the equation[8]

$$I_Q = \frac{KM(\nu_0 - \Delta\nu)^4}{\Delta\nu[1 - \exp(-h\Delta\nu/kT)]}\left[45\left(\frac{6}{6 - 7\rho}\right)\bar{\alpha}'_Q{}^2\right] \quad (1)$$

[1] This investigation was supported by Public Health Service Grant GM-13498 from the National Institute of General Medical Sciences and by National Science Foundation Grant GP-10122.

[2] L. H. Jones, R. S. McDroell, and M. Goldblatt, *Inorg. Chem.*, **8**, 2349 (1969).

[3] (a) G. Pajaro, F. Calderazzo, and R. Ercoli, *Gazz. Chim. Ital.*, **90**, 1846 (1960); (b) G. Cetini and O. Gambino, *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Natur.*, **97**, 1197 (1962–1963).

[4] D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, **8**, 2544 (1969).

[5] (a) H. B. Gray and N. A. Beach, *J. Amer. Chem. Soc.*, **85**, 2322 (1963); (b) N. A. Beach and H. B. Gray, *ibid.*, **90**, 5713 (1968).

[6] A. F. Schreiner and T. L. Brown, *ibid.*, **90**, 3366 (1968).

[7] K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 1273 (1968).

[8] R. E. Hester in "Raman Spectroscopy," H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1967, Chapter 4.

[9] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **32**, 319 (1960).

[10] G. W. Chantry and R. A. Plane, *ibid.*, **34**, 1268 (1961).

[11] T. V. Long, II, and R. A. Plane, *ibid.*, **43**, 457 (1965).

[12] C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **9**, 1045 (1970).