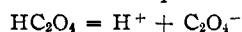


There appears to be no chemically reasonable way of explaining the appearance of hydrogen peroxide if only Mn^{2+} is formed as the reducing intermediate. With the first alternative however, the observation can readily be understood. Two radicals $C_2O_4^{\cdot-}(HC_2O_4)$ or $CO_2^{\cdot-}(HCO_2)$ may be expected to form a peroxide on association. In the acid solutions the peroxalic acid or perdicarboxylic acid would hydrolyze to form hydrogen peroxide and regenerate the organic acid. Hydrogen peroxide is not produced in very acidic solutions presumably because the reducing intermediate reacts rapidly with $MnC_2O_4^+$, and the concentration of this ion increases with increasing acid concentration. At low acid, where the rate of decomposition of the manganese-oxalate complexes is low, the stationary concentration of the organic radicals will be similarly low, and the reaction of the radicals with $Mn(III)$, being first order with respect to the radical concentration, will be favored over the association of the radicals. The decrease in peroxide production as the acidity is decreased however seems too sharp to be completely explained in this way, and it seems possible that effects due to an equilibrium



become important when the hydrogen ion concentration is about 0.5 *M*. This would attribute to

HC_2O_4 a dissociation constant about 0.5, and this value seems not unreasonable in comparison with 1.7×10^{-4} for $HC_2O_4^{\cdot-}$.

Summary

Kinetic data on the oxidation of oxalate by manganic ion over the range 6×10^{-6} *M* oxalate ion to 0.19 *M* oxalate ion are presented. These data are interpreted if it is assumed that the first order decomposition of each of the ions $MnC_2O_4^+$, $Mn(C_2O_4)_2^{\cdot-}$, $Mn(C_2O_4)_3^{\cdot\cdot}$ contributes to the reaction. Values for the specific rates of decomposition of these ions, for the activation energy of the decomposition of $MnC_2O_4^+$ and $Mn(C_2O_4)_3^{\cdot\cdot}$, and for the equilibrium quotients relating the complexes, are presented.

The rate of decomposition of $MnC_2O_4^+$ deduced from experiments on catalysis by manganic ion agrees quantitatively with that directly observed in the present work.

When the oxalate ion concentration is sufficiently great, ca. 0.1 *M*, the rate of reaction is independent of this variable.

Hydrogen peroxide is produced in the oxidation of oxalic acid by manganic ion within a limited acid concentration range, and conclusions about the detailed mechanism of reaction based on this observation are offered.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Phenyl Silicon Isothiocyanates

BY HERBERT H. ANDERSON

Five monoisothiocyanates remain the sole stable members of the corresponding ternary series. They are: $(CH_3O)_3Si(NCS)$,¹ $SiCl_3(NCS)$,¹ $PCl_2(NCS)$,¹ $POCl_2(NCS)$ ¹ and $PF_2(NCS)$.¹

Introduction of the small, neutral methyl group allowed isolation of the first complete ternary series— $(CH_3)_3Si(NCS)$, $(CH_3)_2Si(NCS)_2$ and $(CH_3)Si(NCS)_3$.² Apparently the normal boiling point of the compound was not an important factor in determining stabilities; the "acidity" of the other group seemed to be the criterion.

To test this further, the author has now synthesized a complete series of phenyl silicon isothiocyanates, in which the phenyl groups are definitely more acidic than the neutral methyl groups of the only previously known complete series, and less acidic than methoxyl and the halogens. Moreover, phenyl is a group of rather large molar volume, approximately double that of isothiocyanate.

Steric effects may be encountered in proposed future syntheses of isopropyl and tertiarybutyl

silicon isothiocyanates; the planar phenyl ring was no steric hindrance to introduction of isothiocyanate groups.

Preparation of New Compounds.—Dr. E. G. Rochow of the General Electric Company, Schenectady, N. Y., kindly furnished samples of phenyltrichlorosilane and diphenyldichlorosilane, which were used after distillation at 200–202.5° and 301–303°, respectively. Triphenylchlorosilane, prepared from the diphenyl analog, was distilled at 189° under 3 mm. pressure.

Silver isothiocyanate in 30% excess converted each of the three phenylchlorosilanes, in benzene solution, into the corresponding isothiocyanate; after an hour at 80–90°,³ the suspended silver salts were filtered and washed with benzene. After distillation of benzene at atmospheric pressure, each compound was distilled at 3 mm. pressure through a plain column 4 mm. i. d. and 300 mm. long. Middle fractions used in physical measurements and analyses were collected at the following temperatures: phenyl silicon trisothiocyanate, 153.5–154.5°; diphenyl silicon diisothiocyanate, 173–174°; triphenyl silicon isothiocyanate, 188.5–189.5°. Yields varied from 72 to 90%.

Analyses.—A weighed sample of each compound was decomposed in methanol; after addition of water, thiocyanate was determined by titration with silver nitrate solution in the presence of ferric iron. The slow rate of solution of triphenyl silicon isothiocyanate in methanol

(1) Anderson, *THIS JOURNAL*, **67**, 223, 2176 (1945); **69**, 2495 (1947).

(2) Anderson, *ibid.*, **69**, 3049 (1947).

(3) Forbes and Anderson, *ibid.*, **62**, 761 (1940).

TABLE I
 DATA ON PHENYL SILICON ISOTHIOCYANATES

Compound	(C ₆ H ₅) ₁ Si	(C ₆ H ₅) ₂ Si(NCS)	(C ₆ H ₅) ₃ Si(NCS) ₂	(C ₆ H ₅) ₃ Si(NCS) ₃	Si(NCS) ₄
Boiling point, °C.	428 ^a	396 ± 1.5	376 ± 1.5	339.6 ± 1	314.2 ⁷
B. p. calcd., ⁸ °C.	..	399.5	371	342.5
M. p., °C.	233 ^a	76 ± 1	46 ± 1	52 ± 1	143.2 ⁷
Density at (T) ^o C., in solution	1.188 (30)	1.291 (31)	1.41 (20)
Log P = A { A	..	8.2182	8.9132	8.7676	8.4484 ²
- B/T { B	..	3572	3913	3607	3276
ΔH calcd., kcal./mole	..	16.3	17.9	16.5	13.9 ²
Trouton constant	..	24.4	27.6	26.9	23.7 ²
Rate of hydrolysis in pure water	Inert	Practically inert	Moderate	Moderate	Rather rapid

was a hindrance. In two cases silica was obtained, with some difficulties, by hydrolysis, oxidation with nitric or sulfuric acids, and ignition. One compound was burned in oxygen in a tube containing lead chromate and silver wire, and hydrogen estimated thereby. Molecular weights, obtained through lowering of the freezing point of camphor, confirmed monomeric formulas. Calcd. for (C₆H₅)₁Si(NCS)₃: NCS, 62.4; Si, 10.0; mol. wt., 279.4. Found: NCS, 62.0, 61.5; Si, 10.0; mol. wt. 318. Calcd. for (C₆H₅)₂Si(NCS)₂: NCS, 38.9; Si, 9.4; mol. wt., 298.4. Found: NCS, 38.7; Si, 9.5; mol. wt., 307. Calcd. for (C₆H₅)₃Si(NCS): NCS, 18.3; H, 4.8; mol. wt. 317.4. Found: NCS, 18.2, 18.1; H, 4.9; mol. wt., 296.

Physical Properties (see Table I).—Dynamic vapor pressure measurements were made on the day of final purification, with calibrated mercury thermometers, and according to the method described by Mack and France.⁴ Heats of vaporization and Trouton constants were calculated from the data.

Supercooling, apparently characteristic of compounds of this general type, occurred to the following extents: monophenyl, 52°; diphenyl, 46°; triphenyl, 20°. After formation of crystals during vigorous stirring, the samples showed rather sharp freezing points and melting points.

All the purified compounds were colorless. A solution of diphenyl silicon diisothiocyanate in phenyl silicon triisocyanate⁵ furnished, upon application of the law of mixtures, a molar refraction (*n*² formula) of 90.1 ml., compared with 90.0 ml. calculated for (C₆H₅)₂Si(NCS)₂ and 85.5 ml. calculated for (C₆H₅)₂Si(SCN)₂. Assumptions made previously² were followed in these estimations of molar refractions.

Chemical Properties.—Tetraphenylsilane was inert to pure water; triphenylsilicon isothiocyanate was practically inert, since a sample stood for a week in open air during the summer without discoloration; the diisothiocyanate, triisothiocyanate and tetraisothiocyanate hydrolyzed with progressively increasing ease in water.

Benzene and carbon tetrachloride were good solvents for these isothiocyanates. Ethanol dissolved readily all save the triphenyl compound,

which dissolved slowly even in methanol. Decomposition occurred, of course.

Discussion

1. A provisional conclusion from the existing information is that the stability of mixed isothiocyanates is associated with the "acidity" of the other group attached to the central atom rather than with the molar volume of that group, or the normal boiling point of the compound. Neutral methyl and the slightly acidic phenyl permit complete series, whereas acidic methoxyl, chloride and fluoride allow only monoisothiocyanate derivatives. (The investigation of possible steric effects is planned.) At this time the existence of certain new related isothiocyanates is known: benzyl silicon triisothiocyanate, *n*-butyl silicon triisothiocyanate and triethoxy silicon isothiocyanate, of boiling points 349°, 300° and 206°, respectively. The stability of the last three compounds is consistent with the interpretation made in this paragraph.

2. Supercooling is encountered in the phenyl silicon isothiocyanates, while the analogous methyl silicon isothiocyanates do not do this.²

3. Triphenyl silicon isothiocyanate resists hydrolysis almost as markedly as does the inert tetraphenylsilane.

The author thanks Professor George S. Forbes of this Laboratory for sustained interest in these investigations.

Summary

1. Phenyl silicon isothiocyanates were formed through reaction of silver (iso)thiocyanate with phenylchlorosilanes. All three possible ternary compounds were isolated: phenyl silicon triisothiocyanate, (C₆H₅)₁Si(NCS)₃, melting at 52° and boiling at 340°; diphenyl silicon diisothiocyanate, (C₆H₅)₂Si(NCS)₂, melting at 46° and boiling at 376°; triphenyl silicon isothiocyanate, (C₆H₅)₃Si(NCS), melting at 76° and boiling at 396°.

2. Measurements of physical properties included vapor pressures, and two densities and one molar refraction obtained in solution. The resistance of triphenyl silicon isothiocyanate to hydrolysis was striking.

3. All the evidence available at present indicates that the non-existence of certain diisothio-

(4) Mack and France, "Laboratory Manual of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1934, p. 47.

(5) Forbes and Anderson, *THIS JOURNAL*, **70**, (1948).

(6) Lewis and Newkirk, *ibid.*, **69**, 701 (1947).

(7) Reynolds, *J. Chem. Soc.*, **89**, 397 (1906).

(8) Swarts rule, Swarts, *Bull. soc. chim.*, **35**, 1557 (1924).

cyano and triisothiocyano compounds is associated with the electrical configuration (acidity) of the other group attached to the central atom

rather than with either the molar volume of the group or the boiling point of the compound itself. CAMBRIDGE, MASSACHUSETTS RECEIVED OCTOBER 1, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Methyl Silicon Isocyanates and *n*-Butyl Silicon Triisocyanate

BY GEORGE S. FORBES AND HERBERT H. ANDERSON

This paper on the methyl silicon isocyanates describes the first isolation of organosilicon pseudo halides; the introduction of methyl groups into silicon tetrakisocyanate was first attempted, unsuccessfully, using methylmagnesium iodide, and also dimethylmercury. All three methyl silicon isocyanates and also *n*-butyl silicon triisocyanate were then prepared through reaction of silver isocyanate with the appropriate alkylchlorosilanes, with yields of at least eighty per cent.

Preparation of Alkyl Silicon Isocyanates.—The homogeneity of their reaction products indicated that the methylchlorosilanes, obtained from the Dow Corning Corporation of Midland, Michigan, had been carefully purified. A thirty-gram sample of each methylchlorosilane was treated with a 25% excess of silver isocyanate, added in three portions; benzene was the solvent used in preparation of the monomethyl and dimethyl compounds, while isopropylbenzene proved more suitable for the trimethyl derivative. After the usual half-hour at 90°,¹

(CH₃)₂Si(NCO)₂, 138.3–138.5° at 760 mm.; (CH₃)₃Si(NCO), 90.5–90.8° at 760 mm.

n-Butyltrichlorosilane, prepared from tetrachlorosilane and the alkylmagnesium bromide and boiling at 148.7–149.3°, was gradually added to an excess of silver isocyanate suspended in benzene, in a reaction of moderate vigor. The middle fraction, boiling at 134.6–135.4° under 59 mm., was used for all measurements.

Chemical Properties.—The monoisocyanate floats on water and hydrolyzes slowly at the interface; the diisocyanate hydrolyzes slowly at first and finally at a moderate rate. *n*-Butyl silicon triisocyanate hydrolyzes at a moderately fast rate; when shaken with an equal volume of water, the temperature rise is only about 20°—much less than in the vigorous hydrolysis of silicon tetrakisocyanate.

These four new liquids are easily soluble in petroleum ether (30–60°), carbon disulfide, carbon tetrachloride, benzene and isopropylbenzene.

TABLE I
DATA ON ALKYL SILICON ISOCYANATES

Compound	(CH ₃) ₁ Si ²	(CH ₃) ₂ Si(NCO)	(CH ₃) ₂ Si(NCO) ₂	(CH ₃) ₃ Si(NCO) ₃	Si(NCO) ₄ ¹	(ⁿ C ₄ H ₉) ₃ Si(NCO) ₃
B. p., °C.	26.5	91.0 ± 0.3	139.2 ± 0.3	170.8 ± 0.3	185.6 ± 0.5	215.5 ± 0.5
M. p., °C.	−49.0 ± 3	−31.2 ± 3	2.7 ± 0.5	26	−37 ± 3 ^b
Refractive index at 20° (Abbe) = 0.0010	1.3591	1.3960	1.4221	1.4430	1.4610	1.4479
<i>d</i> ²⁰ ₄ , found	0.6464	0.867	1.076	1.267	1.442 ^a	1.141
Molar refraction, ml.	{ Found 30.02 Calcd. (30.02)	{ Found 31.92 Calcd. 31.84	{ Found 33.60 Calcd. 33.66	{ Found 35.39 Calcd. 35.47	{ Found 37.29 Calcd. (37.29)	{ Found 48.53 Calcd. 49.34
Log P = A − B/T { A B	7.8446	8.1540	8.4150	9.0198	8.4830
Δ <i>H</i> vap. (calcd.), kcal.	8.3	10.0	11.2	12.9	12.5
Trouton constant	22.7	24.1	25.3	26.5	25.6
Molecular wt. { (Dumas) { Found Calcd.	{ 117.5 115.2	{ 146.5 142.2	{ 176 169.1	{ 204 196	{ 225 211.2
Carbon, % ³ { Calcd.	{ 41.6 41.7	{ 33.7 33.8	{ 28.1 28.4	{	{
Hydrogen, % ³ { Calcd.	{ 8.1 7.9	{ 4.4 4.3	{ 1.6 1.8	{	{ 4.0 4.3
Nitrogen, % { (Dumas) { Found Calcd.	{ 12.0 12.2	{ 19.5 19.7	{ 25.0 24.8	{	{ 20.3 20.0

^a Calculated from *D*²⁵₄ of 1.434. ^b Forms glass persistently; difficult to convert glass to crystalline solid.

the suspension of silver salts was filtered and washed. After distilling off the benzene, the triisocyanate and diisocyanate were recovered; the monoisocyanate was distilled directly from the higher-boiling isopropylbenzene. Each individual compound was distilled at least twice in a plain column, 4 mm. i. d. and 500 mm. long, and final fractions were taken at the following (uncorrected) temperatures: (CH₃)Si(NCO)₃, 169.2–169.6° at 755 mm.;

Physical Properties (See Table I).—All four compounds were colorless liquids. The vapor of trimethyl silicon isocyanate was nauseating and also very easily inflammable. Dynamic

(2) Bygden, *Z. physik. Chem.*, **90**, 243 (1915). Index and density at 18.7°.

(3) Combustions in oxygen with lead chromate and silver wire in tube. See Elving and McElroy, *Ind. Eng. Chem., Anal. Ed.*, **13**, 660 (1941).

(1) Forbes and Anderson, *THIS JOURNAL*, **62**, 761 (1940).