[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Exchange Reactions in Volatile Isocyanates and Isothiocyanates of Silicon, Germanium and Phosphorus

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Derivatives of silicon, germanium and phosphorus often readily exchange isocyanate and isothiocyanate, also sulfate and mercaptoacetate, groups for chlorine and bromine (bromine does not replace isocyanate) at the boiling points of homogeneous, primarily covalent liquid solutions. Reactions occur among derivatives of silicon, germanium and phosphorus, or between one of these derivatives and aluminum chloride, benzoyl chloride, or sometimes even sulfur monochloride, mercuric chloride, titanium tetrachloride and arsenic trichloride. This process for isocyanates and isothiocyanates—contradicting previous reactions with silver halides, sulfide, isocyanate, isothiocyanate and (iso)cyanide—follows a previously-known "volatility principle," wherein the most volatile component distils from the system. Table I lists almost forty successful exchange reactions, examples of which are $C_6H_5PCl_2 + n\text{-PrSi(NCS)}_3 \rightarrow C_6H_5P(NCS)_2 + n\text{-PrSiCl}_3$ and $PO(NCS)_3 + n\text{-}C_{12}H_{25}SiCl_3 \rightarrow POCl_3 + n\text{-}C_{12}H_{25}Si(NCS)_3$.

Prior to this study definite rules[1] covered reactions of organosilicon halides, sulfides, isocyanates, isothiocyanates and (iso)cyanides; these rules were in reasonable agreement with each other, and are not repeated herein.

Before the present paper it was not possible to convert compounds such as $Si(NCO)_4$, $Si(NCS)_4$, $Ge(NCO)_4$ or $EtGe(NCO)_3$ into the corresponding chlorides by any one-step reaction. Thus the recovery of precious germanium compounds was strongly hampered.

This present paper demonstrates successful exchange reactions in which chlorine replaces isocyanate or isothiocyanate, and in which bromine replaces isothiocyanate; in trialkylsilicon derivatives the "volatility series," in order of increasing volatility, is $HNC_6H_5 \rightarrow NCS \rightarrow I \rightarrow NCO$ and $Br \rightarrow Cl$. The most volatile compound is allowed to distil out of the system under gentle reflux. In trialkylgermanium derivatives there is a "volatility series" $SO_4 \rightarrow SCH_2COO \rightarrow Br \rightarrow Cl$, the chloride being the most volatile. A general "volatility principle" for volatile compounds has been known for many years, and should not be considered new in this paper; rather, the apparently novel feature is the application of this "principle" to isocyanates and isothiocyanates of silicon, germanium and phosphorus.

This paper also studies the scope of exchange reactions occurring with isocyanates, isothiocyanates and a few related derivatives of silicon, germanium and phosphorus. In this study emphasis is placed upon halides which react with the aforesaid isocyanates and isothiocyanates—or which fail to react with them. When there is an extreme difference in volatility a greater number of chlorides will react with a given compound than otherwise; for example, $(CH_3)_2Si(HNC_6H_5)_2$ yields $(CH_3)_2SiCl_2$ when heated with arsenic trichloride or antimony trichloride. Antimony trichloride does not react with $Si(NCS)_4$ or $Si(NCO)_4$.[1]

Practically all the evidence herein indicates that the reported exchange reactions occur in the *liquid phase*, and among *primarily covalent* compounds. The exchanges do not occur with primarily ionic compounds; the silver salts are at least partly ionic and may have important lattice energies which can direct the nature of reactions. Reactions with silver salts do not follow a "volatility principle," since less volatile isocyanates and isothiocyanates are produced from chlorides of silicon, phosphorus and germanium.[1]

A study of the exchange reactions of silicon, germanium and phosphorus derivatives containing isocyanate and isothiocyanate—see Table I—seems to indicate that these reactions occur readily with elements in the center part of the Mendeleeff periodic table, usually of comparable covalent single bond radii. Exchanges occur most readily with halides of aluminum, silicon or phosphorus; less readily with a germanium halide or an organic halogen adjacent to a carbonyl group (benzyl chloride does not react); still less readily with mercuric halides; sometimes even with halides such as sulfur monochloride, titanium tetrachloride, arsenic trichloride and antimony trichloride.

Chlorine transfers from phosphorus to silicon in the reaction $C_6H_5PCl_2 + n\text{-PrSi(NCS)}_3 \rightarrow C_6H_5P(NCS)_2 + n\text{-PrSiCl}_3$; chlorine transfers from silicon to phosphorus—in the opposite direction—in the reaction $PO(NCS)_3 + n\text{-}C_{12}H_{25}SiCl_3 \rightarrow POCl_3 + n\text{-}C_{12}H_{25}Si(NCS)_3$. Thus there is a possibility of making replacements in either direction. Neglecting a slight change in electrical character, phenylphosphorus dichloride and phosphorus trichloride differ only in the respective boiling points, 225° and 75°. In the previous equation phosphorus trichloride, b.p. 75°, could not serve in preparing $n\text{-PrSiCl}_3$, b.p. 126°, from the corresponding isothiocyanate, since phosphorus trichloride would be the most volatile component and would not react.

An earlier paper on the reactions of alkylanilinosilanes[2] suggested the present investigation, and also contained most of the evidence regarding the anilino group.

Isocyanates and isothiocyanates probably react with aluminum chloride in the liquid phase. Aluminum chloride is a catalyst for redistribution which permits migration of alkyl groups at a rate of approximately 1–2%/hour at 300° in methylchlorosilanes.[3] However, the exchange reactions in Table I herein using aluminum chloride go essentially to completion within five minutes at 200° or less; thus the alkyl groups do not migrate in Table I because the reactions in Table I occur approximately

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[1] H. H. Anderson, THIS JOURNAL, **72**, 2761 (1950); C. Eaborn, *J. Chem. Soc.*, 3077 (1950).

[2] H. H. Anderson, THIS JOURNAL, **73**, 5802 (1951).

[3] R. O. Sauer and E. M. Hadsell, *ibid.*, **70**, 3590 (1948); P. D. Zemany and F. P. Price, *ibid.*, **70**, 4222 (1948).

TABLE I

EXCHANGE REACTIONS

Starting materials				Reaction products				
				Most volatile member				
Compound	Wt., g.	Compound	Wt., g.	Compound	B.p., °C.	Wt., g.	Residue	Yield, %
n-PrSi(NCS)$_3$[6]	0.49	PhCOCl	1.51	n-PrSiCl$_3$	124	0.22	PhCO(NCS)	62
n-PrSi(NCS)$_3$	.61	HgCl$_2$	2.2	n-PrSiCl$_3$	125	.28	Hg(NCS)$_2$	65
n-PrSi(NCS)$_3$	.54	PhPCl$_2$	1.10	n-PrSiCl$_3$	124	.24	PhP(NCS)$_2$	60
i-PrSi(NCS)$_3$[6]	.54	PhPCl$_2$	0.94	i-PrSiCl$_3$	124	.12	PhP(NCS)$_2$	30
EtSi(NCS)$_3$[7]	.76	S$_2$Cl$_2$	1.68	EtSiCl$_3$	98	.47	(S–SCN)$_x$[13]	87
EtSi(NCS)$_3$	.45	AlCl$_3$	1.0	EtSiCl$_3$	96	.21	Al(SCN)$_3$	70
Et$_2$Si(NCS)$_2$[7]	.49	PhPCl$_2$	0.62	Et$_2$SiCl$_2$	130	.29	PhP(NCS)$_2$	75
Et$_3$Si(NCS)[7]	.61	PhPCl$_2$	0.62	Et$_3$SiCl	143	.30	PhP(NCS)$_2$	60
Me$_3$Si(NCS)[8]	.47	S$_2$Cl$_2$	1.17	Me$_3$SiCl	58	.30	(S–SCN)$_x$	77
Me$_3$Si(NCS)	.47	TiCl$_4$	1.21	Me$_3$SiCl	58	.17	Ti(SCN)$_4$	40
(MeO)$_3$Si(NCS)[9]	.18	S$_2$Cl$_2$	0.84	(MeO)$_3$SiCl	109	.09	(S–SCN)$_x$	50
(MeO)$_3$Si(NCS)	.86	PhPCl$_2$	2.03	(MeO)$_3$SiCl	110	.56	PhP(NCS)$_2$	73
Et$_3$Ge(NCS)[10]	.47	PhPCl$_2$	1.10	Et$_3$GeCl	180	.31	PhP(NCS)$_2$	75
PO(NCS)$_3$[11]	.61	PhCOCl	1.6	POCl$_3$	104	.24	PhCO(NCS)	56
PO(NCS)$_3$	.61	HgCl$_2$	2.6	POCl$_3$	103	.30	Hg(SCN)$_2$	72
PO(NCS)$_3$	.61	DodSiCl$_3$	1.30	POCl$_3$	103	.23	DodSi(NCS)$_3$	56
Me$_3$Si(NCS)	.62	SiBr$_4$	2.25	Me$_3$SiBr	80	.64	Si(NCS)$_4$	100
EtSi(NCS)$_3$	.59	BzSi(NCO)$_3$	0.93	EtSi(NCO)$_3$	191	.30	BzSi(NCS)$_3$	64
MeSi(NCS)$_3$	.63	BzSi(NCO)$_3$	1.23	MeSi(NCO)$_3$	179	.32	BzSi(NCS)$_3$	50
Me$_3$Si(NCS)	.47	DodSiI$_3$	2.09	Me$_3$SiI	108	.39	DodSi(NCS)$_3$	61
Me$_2$Si(HNPh)$_2$[4,12]	1.1	PhSi(NCS)$_3$	1.6	Me$_2$Si(NCS)$_2$	212[a]	.60	PhSi(HNPh)$_3$	75[a]
Me$_2$Si(HNPh)$_2$	0.75	Ph$_2$Si(NCO)$_2$	1.32	Me$_2$Si(NCO)$_2$	148	.16	Ph$_2$Si(HNPh)$_2$	40
Me$_2$Si(HNPh)$_2$	.57	SbCl$_3$	2.8	Me$_2$SiCl$_2$	72	.10	Sb(HNPh)$_3$	30
Me$_2$Si(HNPh)$_2$	.63	AsCl$_3$	1.95	Me$_2$SiCl$_2$	71	.31	As(HNPh)$_3$	92
n-PrSi(NCO)$_3$[6]	.54	AlCl$_3$	1.5	n-PrSiCl$_3$	123	.31	Al(NCO)$_3$	90
Ge(NCO)$_4$[13]	.88	PhPCl$_2$	1.56	GeCl$_4$	87	.60	PhP(NCO)$_2$	78
Si(NCO)$_4$[14]	.79	PhPCl$_2$	1.88	SiCl(NCO)$_3$ + SiCl$_2$(NCO)$_2$	140–163	.54	PhP(NCO)$_2$	35 each
Si(NCO)$_4$	1.00	PhCOCl	2.80	SiCl(NCO)$_3$	152	.28	PhCO(NCO)	28
P(NCO)$_3$[14]	0.77	PhCOCl	2.42	PCl$_2$(NCO)	104	.41	PhCO(NCO)	59
P(NCO)$_3$	0.77	HgCl$_2$	2.8	PCl$_2$(NCO) + PCl(NCO)$_2$	120–128	.27	Hg(NCO)$_2$	20 each
P(NCO)$_3$	0.69	AlCl$_3$	1.5	PCl$_3$	75	.36	Al(NCO)$_3$	60
GeBr$_4$	1.13	PhPCl$_2$	1.87	GeCl$_4$[a]	95	.37	PhPBr$_2$	57
SiBr$_4$	1.63	PhPCl$_2$	1.95	SiCl$_4$	62	.53	PhPBr$_2$	66
n-PrSiI$_3$[15]	1.27	PhPCl$_2$	1.05	n-PrSiCl$_3$	123	.40	PhPI$_2$	82
(Et$_3$Ge)$_2$SO$_4$[16]	0.65	HgCl$_2$	1.5	Et$_3$GeCl	173	.37	HgSO$_4$	60
(Et$_3$Ge)$_2$SCH$_2$COO[17]	.49	HgCl$_2$	1.9	Et$_3$GeCl	172	.37	Hg(SCH$_2$COO)	80
(n-Pr$_3$Ge)$_2$SO$_4$[18]	.38	HgBr$_2$	0.70	n-Pr$_3$GeBr	238	.21	HgSO$_4$	48

[a] Impure product; Me$_2$Si(NCS)$_2$ contains PhNH$_3$SCN to extent of approximately 25%; this sample of GeCl$_4$ contains some partly-stable GeCl$_3$Br.

a thousand times as fast as redistributions with migration of alkyl groups.[3]

All these reactions in Table I occur during removal of the most volatile component by distillation; these same reactions may not take place in a sealed tube at elevated temperature, since the volatility of each compound is not a factor when escape is impossible.

In the reaction $CH_3SiI_3 + CH_3SiCl_3 \rightleftarrows CH_3SiCl_2I + CH_3SiClI_2$ the alkyliodochlorosilanes are formed at a rate of 3%/hour at 300°[4]; at equilibrium all four compounds are present in random distribution. Taking a reaction from Table I herein, the equivalent redistribution reaction—which does not occur—would be $SiBr_4 + C_6H_5PCl_2 \rightleftarrows SiCl_4 + SiCl_3Br + SiCl_2Br_2 + SiClBr_3 + C_6H_5PBr_2$, assuming C_6H_5PBrCl to be absent. Both higher reaction rates and the predominant absence of mixed halides seem to differentiate the exchange reactions in Table I from the numerous instances of random distribution in uncatalyzed equilibrium mixtures.[4,5]

Experimental

Reactions which went slightly included the following: phenylphosphorus dichloride and either

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(4) H. H. Anderson, THIS JOURNAL, **73**, 5804 (1951); **66**, 934 (1944).

(5) G. Calingaert and others, *ibid.*, **61**, 2748, 2755, 2758, 3300 (1939); **62**, 1099, 1104 (1940).

(6) H. H. Anderson, *ibid.*, **72**, 196 (1950).

(7) *Ibid.*, **71**, 1801 (1949).

(8) *Ibid.*, **69**, 3049 (1947).

(9) *Ibid*, **67**, 2176 (1945).

(10) *Ibid.*, **73**, 5439 (1951).

(11) *Ibid.*, **64**, 1757 (1942).

(12) E. Larsson and B. Smith, *Acta Chem. Scand.*, **3**, 487 (1949); *C. A.*, **44**, 1897 (1950). Reference 4 should have listed this.

(13) G. S. Forbes and H. H. Anderson, THIS JOURNAL, **65**, 2271 (1943).

(14) *Ibid.*, **62**, 761 (1940).

(15) H. H. Anderson, *ibid.*, **73**, 2351 (1951).

(16) *Ibid.*, **72**, 194 (1950).

(17) *Ibid.*, **72**, 2089 (1950).

(18) *Ibid.*, **73**, 5798 (1951).

n-propyltriisocyanatosilane or *n*-butyltriisocyanatosilane, both of which gave approximately 20% yields of partially-chlorinated compounds; tetrabromosilane and *n*-dodecyltrichlorosilane, which furnished a 10% yield of tribromochlorosilane.

Reactions which included decomposition resulted when sulfur monochloride was warmed with dimethyldianilinosilane or with *n*-dodecyltriiodosilane; the former yielded a dark mess, while the organosilicon iodide reacted to liberate much iodine, showing the non-existence or very low stability of a sulfur iodide.

No reaction or an extremely slow reaction occurred in the twenty-three following instances: $Ge(NCO)_4$ and $HgCl_2$ or $AsCl_3$ or $n\text{-}C_{12}H_{25}SiCl_3$ or S_2Cl_2; $Si(NCO)_4$ and $TiCl_4$; $EtSi(NCO)_3$ and $HgCl_2$; $C_7H_7Si(NCO)_3$ and diphenylsilane; $(MeO)_2Si(NCO)_2$ and S_2Cl_2; $EtOSi(NCO)_3$ and $PhPCl_2$ or PhCOCl or $AlCl_3$ or $n\text{-}C_{12}H_{25}SiCl_3$; $MeSi(NCS)_3$ and $AsCl_3$ or $GeBr_4$; $Me_3Si(NCS)$ and $AsCl_3$ or $GeBr_4$; $Et_3Si(NCS)$ and NH_4Cl or $PhBCl_2$ or diphenylsilane; $n\text{-}PrSi(NCS)_3$ and $PhCH_2Cl$ or $PbCl_2$; $i\text{-}PrSi(NCS)_3$ and $PhBCl_2$; $GeBr_4$ and $n\text{-}C_{12}H_{25}SiCl_3$. Mr. Robert C. West, Jr., of Harvard University kindly furnished the sample of diphenylsilane, a liquid of b.p. about 270°. Table I includes the abbreviations Ph for phenyl, Dod for dodecyl and Bz for benzyl, also those for methyl, ethyl, propyl and butyl.

Experimental Method.—The same small distillation units, of five theoretical plates, used previously with reactions of anilinosilanes[2] were used; 0.5–4.0 ml. of liquid could be used in equipment which may be described elsewhere at a later date. A solid such as mercuric chloride was weighed and then transferred into the distilling unit before addition of the liquid halide or ester. An uncalibrated microchemical transfer pipet and a calibrated syringe served adequately for the transfer of all liquid samples. After the transfer, the two starting compounds in each reaction in the table were brought to a gentle reflux such as would allow escape of the relatively-pure most volatile component at the top of the distilling unit—using a microburner. In both the collection and quantitative estimation of the newly-formed most volatile member a calibrated one-ml. test-tube was adequate. True boiling points often could be obtained only by transferring the distillate to an uncalibrated test-tube and then remeasuring. Most heating periods were 5–10 minutes. Weights of products depended on volumes and available densities. Starting materials consisted of pure isocyanates and isothiocyanates, in sealed tubes, from previous researches; of commercially available compounds such as benzoyl chloride; of phenylphosphorus dichloride, kindly furnished by Victor Chemical Works, Chicago 4, Ill. Reaction residues were not investigated further.

PHILADELPHIA 4, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Silicides of Rhenium[1-3]

BY ALAN W. SEARCY AND ROBERT A. MCNEES, JR.[4]

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Two new rhenium silicides, Re_3Si and ReSi, have been prepared and identified. The vapor pressures of these phases and of $ReSi_2$ have been measured by the Knudsen effusion method. From the vapor pressures, heats and free energies of formation have been calculated for these phases.

The chemistry of transition metal carbides has been studied extensively and is discussed in most textbooks of inorganic chemistry. Little is known, however, of the chemistry of transition metal silicides. Not even the formulas of the compounds formed by silicon with many of the transition metals are yet known, and apparently no vapor pressures or stability data have been reported. In this research the formulas of the rhenium silicides have been determined and their heats and free energies of formation have been determined from vaporization data.

Phase Study

The existence of $ReSi_2$ and the determination of its crystal structure have been reported by Wallbaum[5]; no other compounds of rhenium with silicon have been reported. Experience with other transition metal systems suggested that other rhenium silicide phases might exist. The X-ray diffraction patterns obtained from mixtures of rhenium and silicon which had been heated to high temperatures were examined for evidence of the existence of other phases. Detailed examples of the use of the method have been given previously.[6]

Experimental

All samples were prepared by direct synthesis. Rhenium metal powder was obtained from the University of Tennessee. It contained 8.2% of impurities which could be driven off by heating at 1000° under vacuum and a small amount of silver which did not interfere with the phase studies, but which was driven off at 1500° before vapor pressures were determined. The silicon powder was obtained from the Union Carbide and Carbon Company. Spectroscopic and X-ray diffraction analyses revealed only a trace of iron in the silicon.

Samples were heated in graphite crucibles. X-Ray diffraction photographs of mixtures of rhenium and graphite powders heated to 1600° showed only the diffraction patterns of the elements. Silicon carbide lines were found in the diffraction patterns of rhenium–silicon samples after heating only if they contained silicon in excess of the atomic ratio 2Si:1Re. This is believed to be the ratio in the most silicon-rich compound formed by rhenium. Reaction with the graphite crucibles, therefore, did not interfere with our studies.

The rhenium-silicon samples did not reach equilibrium even when heated for several days at 1000°, but high silicon samples reached equilibrium when heated for 45 minutes

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(2) This research was supported by the Office of Naval Research.

(3) For tables of data order Document 3710 from American Documentation Institute, % Library of Congress, Washington 25, D. C., remitting $1.00 for microfilm (image 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(4) Purdue Research Foundation Fellow 1950–1952.

(5) H. J. Wallbaum, *Z. Metallkunde*, **33**, 378 (1941).

(6) L. Brewer, A. W. Searcy, D. H. Templeton and C. H. Dauben, *J. Am. Ceram. Soc.*, **33**, 291 (1950).