

dynamic significance, since the activity coefficients of water, hydrazine and the ions are unknown. The experiments, however, indicate that calcium ion forms complexes with hydrazine and ammonia of

very nearly the same degree of stability. Schwarzenbach and Zobist have shown this to be true for nickel and zinc ion.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conversion of Chlorosilanes to Siloxanes by Dimethylformamide

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Solutions of organochlorosilanes in dimethylformamide undergo reaction at their boiling points to replace all the silicon-chlorine bonds with silicon-oxygen bonds, the oxygen coming from the dimethylformamide. The tetrachlorides of silicon and titanium appear to be oxygenated in a similar way. The chlorine appears as dimethylamine hydrochloride, and carbon monoxide is produced at the same time. The reaction is slow at 153° but is complete in two to ten days if 1.6 to 2.0 molecules of dimethylformamide per atom of chlorine have been employed. It is shown that the reaction is not a hydrolysis of the chlorosilane in water produced by condensation of the aldehyde hydrogen with carbonyl groups, for such a "conventional" condensation is neither spontaneous nor brought about by small amounts of hydrochloric acid; even if it had occurred, it could furnish only half of the oxygen required. The molar ratios of products indicate that a condensation of *N*-methyl hydrogen and carbonyl oxygen takes place under the influence of the chlorosilane as a Lewis acid, followed immediately by oxygenation of the chlorosilane and absorption of the chlorine as dimethylamine hydrochloride.

Although silicon tetrahalides and some organochlorosilanes form solid addition compounds with dimethylformamide, $\text{HCON}(\text{CH}_3)_2$ ^{2,3} (hereafter called DMF), many other organochlorosilanes undergo solvolytic dissociation in dimethylformamide to provide highly-conducting solutions.⁴ In order to gain more information concerning the extent of such dissociation in 0.01 to 0.5 *M* solutions, measurements of the elevation of the boiling point of the solvent were undertaken. We were surprised to find that the boiling points of solutions of triphenylchlorosilane in DMF rose continuously, as though more ions were being produced hourly no matter how well the solutions were protected from the atmosphere. Furthermore, after extended periods of boiling such solutions, large crystals of hexaphenyldisiloxane precipitated upon cooling. Since the amounts of water originally present in the DMF would suffice to form only 0.06 to 0.08 g. of hexaphenyldisiloxane, whereas several grams separated, it became evident that the chlorosilane was being oxygenated by the carbonyl oxygen of the amide. This was the more unexpected because ketones are commonly used as solvents for the hydrolysis of chlorosilanes, yet no reaction of the carbonyl group previously had been observed. The new reaction raised the possibility of preparing silicone polymers without the hydrolytic procedure now universally employed, a matter of some interest because polymers prepared under radically different conditions might be expected to be different in their structure and properties.

This paper reports the reactions of ten organochlorosilanes and four Group IV tetrachlorides with DMF. All were refluxed with the DMF for extended periods, and all except tin tetrachloride reacted to exchange their chlorine for oxygen. Although the reactions occurred at different rates, in

all instances where oxygenation occurred dimethylamine hydrochloride was identified as a product. The reaction mixtures also evolved carbon monoxide, and the loss of weight due to such evolution was determined. The course of the general reaction was followed by studying its stoichiometry, and the explanation which follows the Experimental section is based upon the observed molar ratios.

Experimental

DMF.—Specifications for the du Pont dimethylformamide indicated not over 0.15% water; titration with Karl Fischer reagent showed 0.05% in our sample. Drying with calcium hydride caused some decomposition, probably because of the alkalinity of the desiccant. The best method of drying was found to be distillation with reagent-grade benzene, yielding a benzene-free fraction containing (by titration) less than 0.003% water. This dried material was used in all the experiments.

Other Reagents.—Highest-purity mono-, di- and trimethylchlorosilanes were received from the General Electric Company, and all other organochlorosilanes were purchased in purified grades. The triphenylchlorosilane of that grade was found to contain 2% of silicon tetraphenyl, but a single distillation at 378° gave the chlorosilane in 99.5% purity. The other reagents were satisfactory as received.

Procedure.—Solutions of the organochlorosilanes in DMF were prepared at room temperature (at which there was no perceptible reaction) and then were refluxed for extended periods. The proportions and conditions are listed in Table I. Atmospheric moisture was excluded by drying tubes at the ends of the reflux condensers. The cobalt salt present in the indicating Drierite within these tubes was found to be a sensitive indicator of amines evolved through overheating of the solutions or from decomposition of a caked mass in the boiling flask, for the cobalt ion soon formed complexes of characteristic intense blue or green when such amines were present. Such decomposition could be avoided in most instances by using heating mantles operated at minimum temperature.

In several experiments the gas evolved from the reaction mixture was led into two traps, the first cooled to -80° and the second to -196°. No material ever condensed in the first; the colorless liquid that condensed in the second was identified as carbon monoxide by its low boiling point and by its infrared absorption spectrum. Whenever the carbon monoxide was not condensed and collected, the loss of weight of the reaction flask was followed to determine how much carbon monoxide was evolved.

The reaction mixtures were acid at the start, and became alkaline only when all of the Si-Cl bonds were converted to Si-O- bonds. In some instances (see Table I) the precipi-

(1) Procter and Gamble Fellow at Harvard University, 1952-1953.

(2) Kurt Gingold and Eugene G. Rochow, *THIS JOURNAL*, **76**, 288 (1954); T. S. Piper and Eugene G. Rochow, *ibid.*, **76**, 4318 (1954).

(3) Kurt Gingold, *System of Chlorosilanes and Amides*, Thesis, Harvard University, 1953, Chapter 3.

(4) Kurt Gingold, Eugene G. Rochow, Dietmar Seyferth, Albert C. Smith, Jr., and Robert West, *THIS JOURNAL*, **74**, 6306 (1952).

TABLE I
 REACTION OF ORGANOCHLOROSILANES WITH DMF

Exp.	Organo-chlorosilane	Wt., g.	DMF, g.	Molar ratio	Reflux time, hr.	Yield of siloxane, %	Moles DMF per Cl	Note
1	CH ₃ SiCl ₃	46.0	151.6	6.7	113	96	2.23	a
2	(CH ₃) ₂ SiCl ₂	206.4	366.0	2.3	68	64	1.15	b
3	(CH ₃) ₂ SiCl ₂	109.1	255.5	4.1	320		2.05	c
4	(CH ₃) ₂ SiCl ₂	145.3	378.0	4.6	163		2.30	c
5	C ₂ H ₅ SiCl ₂	42.5	146.4	7.7	71	100	2.56	a
6	(C ₂ H ₅) ₂ SiCl ₂	77.6	175.5	4.9	180	90	2.45	c
7	n-C ₃ H ₇ SiCl ₂	66.7	121.3	4.4	132		Inc.	d
8	n-C ₃ H ₇ SiCl ₂	81.3	118.3	3.5	69	105		b,i
9	C ₆ H ₅ SiCl ₂	89.5	223.6	5.7	565	93	1.90	e
10	(C ₆ H ₅) ₂ SiCl ₂	67.2	64.8	3.3	71	100	1.65	
11	(C ₆ H ₅) ₂ SiCl ₂	146.7	167.5	4.0	135			f
12	(C ₆ H ₅) ₂ SiCl ₂	177.4	120.0	2.3	116	57.5	Inc.	g,d
13	(C ₆ H ₅) ₂ SiCl ₂	108.9	99.9	3.2	64	64	Inc.	h
14	(C ₆ H ₅) ₂ SiCl	54.2	46.0	3.4	7	20	Inc.	b
15	(C ₆ H ₅) ₂ SiCl	21.5	35.6	6.7	5	32	Inc.	h
16	(C ₆ H ₅) ₂ SiCl	93.0	156.9	6.8	42	97	6.8	i
17	(C ₆ H ₅) ₂ SiCl	26.9	55.3	8.3	65	97	8.3	i
18	(C ₆ H ₅) ₂ SiCl	50.8	19.9	1.6	63	82	1.90	j,k
19	(C ₆ H ₅) ₂ SiCl	38.3	14.2	1.5	41	79	1.87	j,k
20	C ₆ H ₁₁ SiCl ₂	101.7	130.2	3.8	22		1.27	d
21	C ₁₂ H ₂₅ SiCl ₂	58.6	89.0	6.3	44		2.10	e
22	C ₁₈ H ₃₇ SiCl ₂	119.1	158.5	7.1	331		2.38	

^a Dried silicone resin after washing. ^b In acetophenone solution. ^c Product fractionally distilled to separate pure cyclic siloxanes for identification. ^d Insufficient DMF for complete reaction; products acid. ^e Solid addition compound forms on mixing but decomposes on refluxing. ^f Extensive decomposition due to high reflux temperature (305°). ^g Xylene used as solvent. ^h Insufficient reflux time for complete reaction. ⁱ Carbon monoxide condensed and identified as a product. ^j Product was an insoluble and infusible silicone resin containing unknown proportion of *s*-triphenylbenzene. ^k Final molar ratio corrected for solubility of (C₆H₅)₂Si₂O in ether and for 0.003% water present in DMF.

 TABLE II
 REACTION OF INORGANIC HALIDES WITH DMF

Expt. pound	Com- g.	Wt., g.	DMF, g.	Molar ratio	Reflux time, hr.	Product	Yield, %	Note
23	SiCl ₄	11.0	63.2	13.4	41	SiO ₂ ·H ₂ O	91	a
24	CCl ₄	47.8	28.4	1.3	0.1			b,c
25	TiCl ₄	24.4	134.0	14.3	72	TiO ₂	57	a
26	SnCl ₄	25.9	77.5	10.7	62	SnO ₂ ?	0	d
17	SnCl ₄	29.1	100.4	12.3	144			d
28	HCl	11.0	56.0	2.5	23	Me ₂ NH ₂ Cl	99	a
29	HCl	0.25	61.7	124	62	None		e

^a Same as footnote *e* in Table I. ^b Iron powder added as catalyst. ^c Violent reaction produces a mixture of chlorinated hydrocarbons but no CO, COCl₂ nor C₂N₂. ^d No SnO₂ isolated, but only 85% of DMF recovered and black residue (soluble in acetone) remained. ^e DMF contained 0.02% water; HCl did not bring about any appreciable condensation of the DMF.

tation of insoluble masses which led to local overheating made it necessary to stop the reaction short of completion.

The mixtures that did run to completion invariably became heterogeneous. A solid or liquid siloxane separated, and a dark liquid containing the excess DMF, together with any other solvent and the soluble reaction products, remained below. The unreacted DMF (and any other solvent) was removed from the separated lower layer by distillation, and the dark residue then was extracted with absolute ethanol. Dimethylamine hydrochloride was precipitated from the ethanol extract with ether, and was purified by further precipitations from ethanol until entirely white. Samples of this purified product were analyzed for chlorine by titration with silver nitrate, and one sample also was analyzed for carbon, hydrogen and silicon by combustion at the Massachusetts Institute of Technology.

Anal. Calcd. for (CH₃)₂NH·HCl: C, 29.46; H, 9.88; Cl, 43.55. Found: C, 29.44; H, 9.85; Cl, 43.3 and 43.4.

Dimethylamine hydrochloride was isolated and identified

as a product of every one of the oxygenation reactions. In some instances where decomposition occurred because of local overheating or because very high-boiling compounds were involved, tetramethylammonium chloride and ammonium chloride were formed in minor amounts and were identified by their physical properties and their chlorine contents.

The reactions of SiCl₄, CCl₄, TiCl₄, SnCl₄ and HCl with DMF also were investigated in the manner just described, and the details are given in Table II.

Reactions with Other Amides.—The oxygenation of organochlorosilanes by formamide, acetamide, dimethylacetamide and benzamide also was studied in order to find whether the reaction of carbonyl oxygen in amides is general. Since all the organochlorosilanes used with DMF reacted in uniform manner, it was considered sufficient to investigate the reactions of diphenyldichlorosilane and triphenylchlorosilane with the other four amides, for these two chlorosilanes give crystalline siloxanes that are easily purified and identified. As before, the molar ratios for complete reaction were sought and the products were identified insofar as possible.

Formamide was found to be immiscible with diphenyldichlorosilane and triphenylchlorosilane, but dry pyridine was a suitable solvent. Both chlorosilanes then were oxygenated completely, and ammonium chloride, ammonia and carbon monoxide also were identified as products. No hydrogen cyanide was found, although special efforts were made to detect any that might have been formed. Since dissociation of formamide to ammonia and carbon monoxide at its boiling point was expected⁵ and found, not all of the amide could take part in the oxygenation reaction. The mole ratios obtained therefore were inconclusive.

Acetamide at its melting point was not appreciably miscible with the two phenylchlorosilanes studied, but in pyridine solutions triphenylchlorosilane was oxygenated completely and diphenyldichlorosilane was 70 to 80% oxygenated. No gaseous products were formed. When 4 g. of anhydrous HCl was bubbled into 33 g. of boiling acetamide and the mixture refluxed for 52 hours, acetonitrile, acetic acid and ammonium chloride were identified as products.

Dimethylacetamide converted triphenylchlorosilane to hexaphenyldisiloxane to the extent of 30% in six days. Under the same conditions diphenyldichlorosilane did not yield a precipitate or a separate layer of diphenylsiloxane, but one-third of the dimethylacetamide was used up in the reaction and dimethylacetamide hydrochloride was identified in the products.

Benzamide, in common with the other unsubstituted amides used in this investigation, was immiscible with both phenyl chlorosilanes studied. In pyridine solution triphenylchlorosilane was 78% oxygenated in 4 days, while diphenyldichlorosilane was 34% oxygenated. No volatile products were formed.

Experiments with Aldehydes and Ketones.—Benzaldehyde did not convert any chlorosilanes to siloxanes upon refluxing for 3 or 4 days, and infrared spectra of the cooled solutions showed only the absorption bands of the reagents. When triphenylchlorosilane was refluxed with acetophenone for 67 hours, a small amount of hexaphenyldisiloxane was precipitated. The quantity corresponded to that which would result if the acetophenone contained 0.08% water. However, when mixtures of acetophenone, DMF and an organochlorosilane were refluxed, oxygenation occurred with less than the usual amount of DMF, and *s*-triphenylbenzene was recovered in the products. The triphenylbenzene was identified by its melting point and by analysis.

Discussion

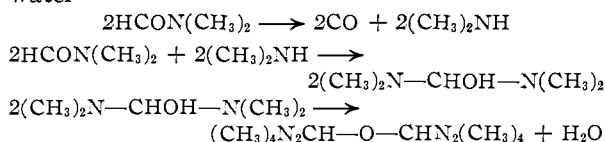
The conversion of an organotrichlorosilane RSiCl₃ to the corresponding siloxane (RSiO_{1.5})₂, whether by hydrolysis or by the action of DMF as described herein, produces an insoluble resinous mass which is difficult to free from other materials and impossible to purify as a pure compound. Organodichlorosilanes R₂SiCl₂ yield some cyclic siloxanes (R₂SiO)₃ and (R₂SiO)₄ that may be separated as chemical individuals, as was done with the dimethyl- and diphenylsiloxanes in this investigation,

(5) P. C. Freer and P. L. Sherman, Jr., *Am. Chem. J.*, **20**, 223 (1898).

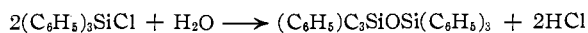
but much linear high-polymeric material that is hard to purify also is formed. On the other hand, triorganomonochlorosilanes R_3SiCl can yield only one product, the corresponding disiloxane $R_3SiOSiR_3$, and this may be isolated as a pure compound. Hence it may be considered a justifiable simplification in the present instance to concentrate the discussion upon the oxygenation of triphenylchlorosilane, since this reaction supplied the most accurate information. As may be seen in Table I, all the other organochlorosilanes reacted with DMF in a similar manner.

Table I shows that in all cases where substantial oxygenation (80% or more) occurred, at least 1.6 moles of DMF per gram-atomic weight of chlorine were consumed. The most reliable figure for the mole ratio is given by the average of experiments 18 and 19 of Table I (conducted with triphenylchlorosilane) in which the requirement is 1.89 molecules of DMF per Si-Cl bond. The first criterion of any interpretation must then be its ability to meet this particular ratio of reactants.

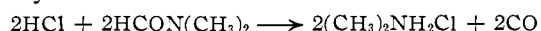
It might be thought that the reaction proceeds through decomposition of the DMF, to dimethylamine and carbon monoxide (possibly aided by a trace of hydrogen chloride), followed by condensation of the dimethylamine with more DMF to form water



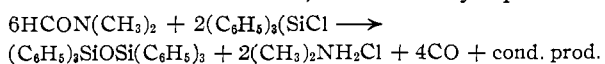
The water would then react rapidly with the chlorosilane



The hydrogen chloride would be taken up immediately by more DMF and, since the mixture is above 90°, the addition product will furnish dimethylamine hydrochloride and carbon monoxide⁶



In this way all of the observed products would be accounted for. However, the summary equation

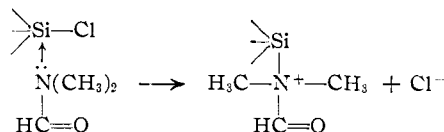


shows that three molecules of DMF per Si-Cl bond are required, whereas the experimental ratio found was 1.89 to 1. Moreover the equation shows two moles of carbon monoxide produced by each mole of triphenylchlorosilane, whereas the observed loss of weight corresponded closely to one mole per mole of the chlorosilane, no matter how large the excess of DMF. Furthermore, the initial decomposition of DMF postulated above begins only at 350°,⁶ whereas the observed reactions took place at reflux temperatures near 151°. The presence of hydrogen chloride does not alter this situation, for reference 6 and our own experiments show that hydrogen chloride ties down the product dimethylamine as its hydrochloride, so that it is not available for the condensation given above. On three counts, then, the "classical" condensation mechanism is impossible.

(6) DMF Product Information Booklet, Grasselli Chemicals Department, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

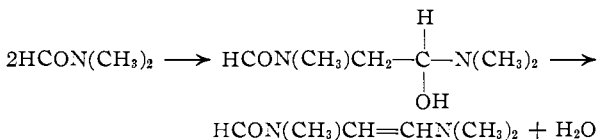
Other mechanisms based on widely-known reactions of amides have been proposed, but all fail by a wide margin to give the large amounts of oxygen and hydrogen required by the observed reaction. Since the phenyl groups bonded to silicon are found to remain intact, the hydrogen of the nitrogen-bonded methyl groups is the only other source of supply.⁷ We propose the following course of reaction based on this premise.

The first step involves coordination of silicon with the nitrogen of the amide, with consequent ionization

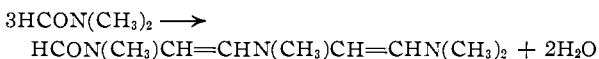


This step is well authenticated by the known extensive solvolytic ionization of all of the organochlorosilanes involved in these experiments,⁴ and by the frequent formation of solid addition compounds of such chlorides with DMF.^{2,3,8} The resulting "quaternization" of the nitrogen atom facilitates transfer of the methyl-bonded hydrogen to oxygen, a reaction that would be very unlikely without the influence of the positive charge.⁹

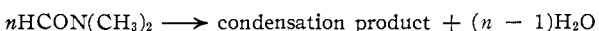
Condensation of methyl hydrogen with carbonyl oxygen then gives the products



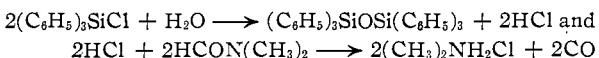
or, with an additional molecule of DMF



In general



It is not necessary that water be formed, but only that the elements of water be available from the condensation for reaction with the chlorosilane. Adopting the convenient fiction of water as an entity in the reaction



as before.

The limiting cases now are apparent. If a very large number of molecules of DMF n condense, $n-1$ approaches n and 0.5 mole of DMF is required to furnish the real or imaginary water for one mole of $(C_6H_5)_3SiCl$. In addition, another mole of DMF is necessary to take up the one mole of HCl formed. The total molar requirement when n is very large therefore is 1.5 moles of DMF. On the other hand,

(7) The "classical" mechanism just given uses all of the aldehyde hydrogen available, and it is insufficient by a factor of two.

(8) It may be considered that all of the reactions of Tables I and II begin with the formation of such a coordination or addition compound, rather than just those in which solid phases first precipitated (experiments 9, 21, 23, 25 and 28).

(9) The authors are indebted to Dr. W. L. Alderson of the du Pont Experimental Station for this important suggestion concerning the effect of the positive charge.

when n is as small as possible ($n = 2$), one mole of DMF is required to furnish the elements of water for one mole of $(C_6H_5)_3SiCl$, and another mole of DMF for the chlorine. At the most, then, the molar ratio will be 2.0.

It will be expected that the actual observed ratio will be between the values 1.5 and 2.0, and will vary from one organochlorosilane to another because the extent of condensation must be dependent upon the reaction temperature and hence upon the boiling point of the chlorosilane. The value of 1.89 for triphenylchlorosilane fits into this view, and should in fact be on the low side because of the high boiling point of this substance. The values near 2.0 for the methylchlorosilanes similarly reflect the low boiling points of these reactants. The value 1.65 for $(C_6H_5)_2SiCl_2$ is considered somewhat less reliable than those for $(C_6H_5)_3SiCl$ because of the described difficulty of purifying the polymeric products, but it falls well within the limits imposed by our condensation. The very large molar ratios in experiments 16 and 17 represent large excesses of DMF used while searching out the molar requirement.

The coordination and condensation proposed here thus accounts for all of the observed products and agrees with the stoichiometry. Whether or not it represents the actual course of the reaction could be tested by using DMF containing deuterium atoms in the methyl groups, for if the condensation proceeds as indicated there should be a quantitative yield of dimethylamine deuteriochloride.

The question of whether or not water actually is formed cannot be settled by the experiments reported herein, nor by the experiment with deuterium. The reactions shown in sequence above must proceed simultaneously, and water need not appear as an entity. We incline toward the view that it does not, since we have found that the proportion of polymeric dimethylsiloxanes obtained from reaction with DMF differs considerably from that obtained by hydrolysis.¹⁰ In effect, the oxygenation with DMF represents a distinctly different method for preparing silicon polymers from their intermediates and may be useful in synthesis on this account.

(10) Extensive fractional distillation of the products of experiments 3 and 4 of Table I showed that only 10% of the mixture of polymers was cyclic tetramer, whereas hydrolysis of the same dimethyldichlorosilane in excess water yields 42% tetramer (W. I. Patnode and D. F. Wilcock, *THIS JOURNAL*, **68**, 358 (1946)). We obtained substantial quantities of higher-boiling cyclics from the DMF reaction.

Of the tetrahalides listed in Table II, silicon tetrachloride may be considered to react by the same mechanism as the organochlorosilanes. Carbon tetrachloride reacts only if iron powder is added, and then in a totally different manner, yielding many chlorinated hydrocarbons. Titanium tetrachloride appears to react in much the same way as silicon tetrachloride, although the reaction did not proceed as far, possibly because its intermediate solid addition compound⁸ is more stable. Tin tetrachloride seemed to react in the same manner and consumed some DMF, but gave no dioxide. Since the free energy of formation of tin dioxide at 25° is only -124.2 kcal. per mole compared with -192.4 kcal. for silicon dioxide, it may be that there is insufficient driving force for reaction in a reasonable time.

Other amides probably warrant as extensive an investigation as DMF, for they show interesting variations. It can only be said at this time that formamide is a more effective oxygenating agent for organochlorosilanes than is acetamide, and dimethylformamide is more effective than dimethyl acetamide. Since benzamide may be condensed to the nitrile and water by a variety of dehydrating agents, it may very well react with organochlorosilanes by such a dehydration, the mechanism proposed for DMF being closed to any unmethylated amide.

Lastly, the behavior of acetophenone is interesting as an example of interaction of two carbonyl compounds under the influence of a chlorosilane. Acetophenone is known to condense with formamide when both are heated with zinc chloride, yielding *sym*-triphenylbenzene.¹¹ We found that acetophenone alone did not condense when heated with chlorosilanes, nor were the latter oxygenated, but when DMF and acetophenone were heated with the same chlorosilanes there was extensive oxygenation with somewhat less than the usual requirement of DMF (experiments 2, 8 and 13). In the same experiments *sym*-triphenylbenzene was identified as a product, as described in the Experimental section. We take this as further indication that silicon chlorides, like zinc chloride, act as Lewis acids in the early stages of the reactions we observed.

We are indebted to the Mallinckrodt Fund at Harvard University for financial aid in obtaining supplies for this investigation.

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(11) M. Reich, *Monatsh.*, **25**, 966 (1904).