[Contribution from the Research and Development Department, Ethyl Corporation]

Studies of Metallosiloxane Polymers

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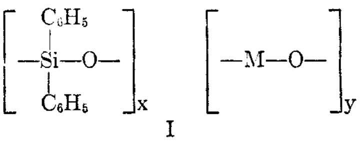
The preparation of some new metallosiloxane polymers has been achieved by the reaction of disodium diphenylsilanediolate with metal chlorides and by the reaction of diphenylsilanediol with metal alkyls. Most of these polymers decomposed rather easily to form siloxane derivatives and metal oxides; in a few cases they were obtained only as short-lived intermediates. The ease of decomposition of these polymers is compared with that of the structurally analogous silicones.

The study of metallosiloxane polymers is of considerable interest due to their possible high thermal stability, particularly in view of the stability of the structurally related silicones.[1] It has been supposed that modifications of the silicone structure by the introduction of other elements into the siloxane chain might result in polymers which are even more stable than the silicones.

Aluminosiloxane,[2] antimonosiloxane,[3] arsonosiloxane,[4] borosiloxane,[5] stannosiloxane[6] and titanosiloxane[2a,6b,7] polymers have been reported. In most of these polymers the hetero elements bear organic substituents, but there have been few reports[2,6a] of metallosiloxanes in which the metal atoms are unsubstituted. In the present work the search for thermally stable polymers has been extended to several new metallosiloxane systems of the type indicated by formula I, where M is Sn, Pb, Mg, Cu, Zn, or Hg.



$$\left[-\overset{C_6H_5}{\underset{C_6H_5}{\overset{|}{\underset{|}{Si}}}}-O-\right]_x\left[-M-O-\right]_y$$

I

Two synthetic approaches were investigated: (1) the reaction of disodium diphenylsilanediolate with metal chlorides, and (2) the reaction of diphenylsilanediol with metal alkyls. The results obtained provide some information concerning the mode of decomposition of these polymers and permit a comparison of their ease of decomposition with that of the silicones.

The reaction of disodium diphenylsilanediolate with stannous chloride gave a stannosiloxane polymer (I. M = Sn); a somewhat similar material had been prepared previously by a different method.[6a] With lead chloride, however, the products were a mixture of a plumbosiloxane polymer (I. M = Pb), a phenyl-substituted cyclic siloxane (II) and lead oxide. Magnesium chloride gave some evidence of metallosiloxane polymer formation, but the products ultimately isolated were the same cyclic siloxane (II) and magnesium oxide. The reaction with cupric chloride proceeded through a short-lived, colored intermediate and gave octaphenylcyclotetrasiloxane and cupric oxide. The product from the reaction with zinc chloride were hexaphenyltrisiloxane-1,5-diol and zinc oxide. With mercuric chloride a colored intermediate was again formed which decomposed to give octaphenylcyclotetrasiloxane; definite evidence for the concurrent formation of mercuric oxide was not obtained.

These results suggest that the reaction of disodium diphenylsilanediolate with metal chlorides proceeds through a polymeric intermediate in which the expected Si—O—M bonds are formed. In most of the cases investigated, however, the polymer easily decomposes to form a siloxane derivative and, except in the case of mercury, the corresponding metal oxide. The isolation of polymers in some cases where the presence of both silicon and the other metal could be confirmed, and the formation of colored intermediates in others, are considered as evidence for this interpretation. In addition, the observation that different metal chlorides lead to different siloxane derivatives indicates that considerably more than simple silanediolate condensation is involved.

Further evidence for these interpretations was obtained from the reaction of diphenylsilanediol with metal alkyls, a reaction which was investigated as another approach to these metallosiloxane polymers. Diethylmagnesium reacted with diphenylsilanediol to form a metallosiloxane polymer (I. M = Mg) which decomposed rather easily upon heating to give the cyclic siloxane (II) and magnesium oxide. Diethylzinc also formed a metallosiloxane polymer (I. M = Zn) which decomposed somewhat less

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(1) D. W. Scott, *J. Am. Chem. Soc.*, **68**, 356 (1946).

(2) (a) K. A. Andrianov, A. A. Zhdanov, N. A. Kurasheva, and V. G. Deluva, *Doklady Akad. Nauk S.S.S.R.*, **112**, 1050 (1957); (b) K. A. Andrianov and A. A. Zhdanov, *Doklady Akad. Nauk S.S.S.R.*, **114**, 1005 (1957); (c) K. A. Andrianov and T. N. Ganina, *Izvest. Akad. Nauk S.S.S.R.*, 74 (1956).

(3) F. A. Henglein, R. Lang, and K. Scheinost, *Makromol. Chem.*, **18-19**, 102 (1956).

(4) R. M. Kary and K. C. Frisch, *J. Am. Chem. Soc.*, **79**, 2140 (1957).

(5) R. W. Upson, U. S. Patent **2,517,945** (1947); F. A. Henglein, R. Lang, and K. Scheinost, *Makromol. Chem.*, **15**, 177 (1953); K. A. Andrianov and L. M. Volkova, *Izvest. Akad. Nauk S.S.S.R.*, 303 (1957); M. G. Voronkov and V. N. Zgonnik, *Zhur. Obschei Khim.*, **27**, 1476 (1957).

(6) (a) F. A. Henglein, R. Lang, and L. Schmack, *Makromol. Chem.*, **22**, 103 (1956); (b) K. A. Andrianov, T. N. Ganina, and E. N. Khrustaleva, *Izvest. Akad. Nauk S.S.S.R.*, 798 (1956).

(7) H. C. Gulledge, U. S. Patent **2,152,058** (1958).

rapidly when heated to give hexaphenyltrisiloxane-1,5-diol and zinc oxide. Since the decomposition products obtained from these polymers are identical to those isolated in the corresponding silanediolate–metal chloride reactions, it appears likely that the silanediolate–metal chloride reactions also proceed through similar polymeric intermediates.

The polymeric nature of the metallosiloxanes isolated was inferred from their resinous nature and from their tendency to form viscous solutions in organic solvents. Cryoscopic molecular weight determinations or solution viscosity measurements could not be made due to a very facile, slight decomposition in solution to form minute quantities of interfering, insoluble solids.[8]

The organic solubility of the polymers isolated which contained both silicon and a hetero metal, and the formation of metal oxides upon their decomposition, strongly indicate that these materials have the metallosiloxane structure.[9] The consistency of the analytical data with this structure in cases where pure polymers were obtained may also be mentioned as evidence for this interpretation. The reaction of alkali metal salts of the mono-functional silanols with metal halides has in fact been shown previously to yield monomeric metallosiloxanes.[10] Determination of structure by infrared study was precluded by the tendency of most of the polymeric products to decompose to a slight extent upon standing to form the interfering, insoluble solids mentioned above.

It is of interest to compare the decomposition of the metallosiloxane polymers with that of the structurally analogous silicones. It appears from the results obtained that the decomposition of the metallosiloxanes investigated in this work occurs by scission of the Si—O—M bonds. This result is quite similar to that observed in the thermal decomposition of linear dimethylpolysiloxanes, which produces cyclic siloxanes,[1,11] apparently by rupture of Si—O—Si bonds. The ease of decomposition of these metallosiloxanes, however, is considerably greater than that of the silicones, implying a lower thermal stability for Si—O—M bonds in these polymers than the Si—O—Si bonds in the silicones. It appears unlikely that the decomposition of the metallosiloxanes could have been caused by hydrolysis or the presence of trace impurities, so the inference that we are dealing here with thermal decomposition seems valid. The slight decomposition of these polymers upon standing, however, could be due to trace impurities or adventitious moisture, but we are inclined to believe that it is a reflection of the possibly different thermal stabilities of the various polymeric fractions.

EXPERIMENTAL[12]

Reaction of disodium diphenylsilanediolate with metal chlorides. A. *With stannous chloride.* To a stirred solution of 9.4 g. (0.05 mole) of anhydrous stannous chloride in 100 ml. of anhydrous acetone was added in portions 13.0 g. (0.05 mol.) of disodium diphenylsilanediolate,[10] and the mixture was refluxed in a dry atmosphere with stirring for 2 hr. The insoluble solids were filtered and washed thoroughly with boiling acetone, then with boiling benzene, and finally with water; evaporation of the aqueous washings gave 5.0 g. of sodium chloride (86%). The 0.1 g. of pale yellow powder remaining after this treatment was shown by qualitative analysis[13] to contain both tin and silicon, a result which was not altered by repeated extraction with boiling benzene.

Evaporation of the combined acetone filtrate and acetone and benzene extracts gave 16.9 g. of a brittle, yellow resin. The resin was dissolved in benzene, filtered to remove traces of insoluble solids, and precipitated by adding the benzene solution to an excess of petroleum ether. There was obtained 14.3 g. (86%) of a stannosiloxane polymer as a light colored powder upon filtration and drying.

Anal. Calcd. for $[(C_6H_5)_2SiO]_5[SnO]_4$: Si, 9.14; Sn, 31.1. Found: Si, 9.20; Sn, 31.0.

The formula $[(C_6H_5)_2SiO]_5[SnO]_4$ indicated by the analysis of course represents an average composition, probably of many molecular species. That tin was incorporated with silicon in a large proportion of these species was indicated by the benzene solubility of the material and by its separation into several fractions, all of which contained both silicon and tin, by numerous reprecipitations from benzene–petroleum ether mixtures.

Reliable values for the molecular weight of this polymer could not be obtained since in solution there was very rapidly formed traces of an insoluble, pale yellow precipitate which was found by analysis[13] to contain both tin and silicon. The resinous nature of the stannosiloxane and its tendency to form viscous solutions, however, indicated that it was undoubtedly polymeric.

The stannosiloxane polymer was stable for 1 hr. up to around 175° when it darkened somewhat. This darkening also occurred at lower temperatures upon longer heating.

B. *With other metal chlorides.* The procedure used in reactions with other metal chlorides was quite similar to that in the above reaction with stannous chloride. Pertinent details are shown in Table I.

Cyclic siloxane (II). Some comment should be made concerning the nature of the cyclic siloxane (II). Its identity as a phenylsubstituted cyclic siloxane was established from its empirical formula and from infrared data. The presence of a strong absorption in the 9.15–9.25 micron region in the infrared, which is characteristic of cyclic siloxanes of larger rings size than the trimer,[14] and the absence of hydroxyl

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(8) The referee has suggested that these solids are probably metal oxides. We are in substantial agreement with this view. In most cases the quantity of solids formed was too small for identification; in a few cases where larger amounts were obtained they were found to be metal oxides.

(9) The referee has pointed out that the metallosiloxane polymers may be considered as metal "salts" of the silanediol. This implies a regularly alternating arrangement of silicon and metal atoms in the polymeric chain. In view of the methods of preparation employed, it seems likely that the polymers first formed must have this structure, but since they decompose to eliminate the elements of a metal oxide it appears that the polymers ultimately isolated are better represented by the more general formula I.

(10) W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, **17**, 1555 (1952).

(11) W. Patnode and D. F. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946).

(12) All melting points are corrected.

(13) The qualitative analyses for the metals were obtained by examination of the emission spectra of the compounds in question.

(14) C. W. Young, *et al.*, *J. Am. Chem. Soc.*, **70**, 3758 (1948).

TABLE I

REACTION OF DISODIUM DIPHENYLSILANEDIOLATE WITH METAL CHLORIDES

Metal Chloride	Mol.[a]	Solvent	Time, Hr.	Temp., °C.	Products[b]	Yield, G.[c]
$PbCl_2$	0.075	Dimethyl sulfoxide	8	80	Plumbosiloxane polymer-cyclic siloxane (II) mixture[d]	20.5
					Lead oxide	2.7
$MgCl_2$	0.05	Acetone	3	Reflux	Cyclic siloxane (II)[e]	2.5
					Magnesium oxide	0.9
$CuCl_2$	0.025	Acetone	2	Reflux	Octaphenylcyclotetrasiloxane[f]	4.2
					Cupric oxide	1.9
$ZnCl_2$	0.025	Acetone	3	Reflux	Hexaphenyltrisiloxane-1,5-diol[g]	1.7
					Zinc oxide	1.9
$HgCl_2$	0.025	Acetone	2	Reflux	Octaphenylcyclotetrasiloxane[f]	3.8
					Inorganic Hg compound[h]	3.9

[a] Equimolar ratios of metal chloride and diol salt were used. [b] NaCl was also a product. [c] The yields given refer to purified products. [d] *Anal.* Found: Si, 8.11; Pb, 30.8. Calcd. values are 6.65% Si and 49.2% Pb for $[(C_6H_5)_2Si—O—Pb—O—]_x$ and 14.16% Si for $[(C_6H_5)_2SiO]_x$. Fractional reprecipitation of mixture from benzene–petroleum ether gave a few mg. of the cyclic siloxane (II), m.p. 187.5–189.5°. [e] Isolated from 10.7 g. of colorless, nearly transparent resin (containing both Mg and Si) by treating the resin with boiling benzene, filtering the MgO formed and recrystallizing the benzene-soluble material from benzene–petroleum ether. M.p. 188–189.5°. *Anal.* Calcd. for $C_{12}H_{10}SiO$: C, 72.67; H, 5.08; Si, 14.16. Found: C, 73.20; H, 5.74; Si, 14.35. [f] Recrystallized from acetone, m.p. 202–202.5°; did not depress mixture m.p. with authentic octaphenylcyclotetrasiloxane. *Anal.* Calcd. for $C_{12}H_{10}SiO$: C, 72.67; H, 5.08; Si, 14.16. Found: C, 72.35; H, 5.44; Si, 13.78. [g] Purified by recrystallization from benzene–petroleum ether, m.p. 111–112°. *Anal.* Calcd. for $C_{36}H_{32}Si_3O_4$: C, 70.55; H, 5.26; Si, 13.75. Found: C, 70.42; H, 5.52; Si, 14.14. Lit. m.p. 111° [C. A. Burkhard, *J. Am. Chem. Soc.*, **67**, 2173 (1945)]. Showed hydroxyl absorption at 2.75–3.00 microns in infrared and the doublet absorption at 9–10 microns characteristic of a linear siloxane [R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 124 (1949)]. [h] Contained 93.2% Hg; insoluble in warm dilute hydrochloric acid, in common organic solvents, and did not contain halogen. Did not appear to be HgO due to its white color and because it left a black residue on ignition.

absorption in the 2.75–3.00 micron region established the cyclic nature of the compound. That it was not identical with hexaphenylcyclotrisiloxane, which melts at 188–189°, was further shown by the fact that a mixture with authentic hexaphenylcyclotrisiloxane[15] melted at 163–169°. Cryoscopic molecular weight determinations in benzene gave the values 532 and 543, but these can be viewed only as indicating an order of magnitude in view of the known difficulties with this determination in the case of phenylsubstituted cyclic siloxanes.[16] Since the compound showed no change of melting point on standing for weeks, it does not appear to be the unstable polymorph of octaphenylcyclotetrasiloxane which melts at the same temperature.[16] The fact that the melting point of the cyclic siloxane (II) is lower than the known stable polymorph[16] of the cyclic tetramer and its markedly greater solubility in acetone further differentiates the two compounds. We conclude that the cyclic siloxane (II) must be at least a pentamer or a cyclic siloxane of even greater ring size.

Reaction of diphenylsilanediol with metal alkyls. A. *With diethylmagnesium.* To a solution of 0.07 mol. of diethylmagnesium[17] in 100 ml. of anhydrous ether was added dropwise with stirring under a nitrogen atmosphere during 1.5 hr. a solution of 15.1 g. (0.07 mole) of diphenylsilanediol in 50 ml. of anhydrous dioxane. Gas evolution was vigorous, and a white precipitate formed during the addition. The reaction mixture was refluxed for 0.5 hr., filtered, and the precipitate was washed with ether. After drying there was obtained 11.1 g. of a white powder which was soluble in dioxane; analysis showed that it contained 10.2% silicon and 15.8% magnesium, a result which corresponds to the average composition $[(C_6H_5)_2SiO][MgO]_{1.8}$. Filtered dioxane solutions on brief standing in an anhydrous atmosphere deposited traces of magnesium oxide which interfered with molecular weight determinations. That the reaction product was probably polymeric, however, was indicated by the formation of viscous solutions by concentration of dioxane solutions of the product under reduced pressure and by the formation of brittle resins upon complete removal of the solvent from these solutions. That the product was not contaminated with siloxanes at this point was shown by the failure to extract any material from the product upon washing it with either acetone, ether, or benzene at room temperature.

The reaction product dissolved in boiling benzene, but shortly thereafter large quantities of white powder separated from the hot solution. Filtration and repeated extraction of the powder with boiling benzene left 2.8 g. of magnesium oxide contaminated with traces of a silicon-containing material.[13] Evaporation of the combined benzene extracts and filtrate and recrystallization of the residue from benzene-methanol gave 3.8 g. of the cyclic siloxane (II) which melted at 189–190° and did not depress a mixture melting point with the cyclic siloxane obtained from the reaction of magnesium chloride and disodium diphenylsilanediolate.

Concentration of the original filtrate from the reaction mixture and extracting the residue from acetone gave an additional 1.2 g. of the cyclic siloxane. The residue remaining after the extraction was largely magnesium oxide.

B. *With diethylzinc.* The reaction of diethylzinc with diphenylsilanediol proceeded quite similarly to that described above. From 18.9 g. (0.154 mol.) of diethylzinc in 300 ml. of dry ether added under nitrogen to 33.2 g. (0.154 mol.) of diphenylsilanediol in 150 ml. of dry dioxane there was obtained after 1 hr. 26.9 g. of a white powder. From this product there was isolated 1.1 g. of hexaphenyltrisiloxane-1,5-diol, m.p. 111–112° (which did not depress a mixture melting point with the diol obtained from the reaction of zinc chloride and disodium diphenylsilanediolate), by extraction with ether and recrystallization from benzene–petroleum ether. The extracted powder contained 8.66% silicon and 27.36% zinc, which corresponds rather closely to the average composition $[(C_6H_5)_2SiO][ZnO]_{1.35}$. It was insoluble in most of the common solvents but dissolved in dimethyl sulfoxide. Dimethyl sulfoxide solutions of this

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(15) Purchased from Anderson Chemical Co., Weston, Mich.

(16) J. F. Hyde, *et al.*, *J. Am. Chem. Soc.*, **69**, 488 (1947) and references cited therein.

(17) J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Am. Chem. Soc.*, **78**, 1221 (1956).

material, however, deposited traces of zinc oxide on brief standing in an anhydrous atmosphere which interfered with molecular weight determinations. That the product was probably polymeric, however, was indicated by the formation of viscous solutions upon concentration of dimethyl sulfoxide solutions of the reaction product under reduced pressure.

Repeated extraction of the reaction product with boiling benzene eventually gave 9.2 g. of hexaphenyltrisiloxane-1,5-diol and left 10.2 g. of zinc oxide contaminated with traces of a silicon-containing compound.

Evaporation of the original filtrate from the reaction mixture and reprecipitating the residue from benzene–petroleum ether gave 9.0 g. of a white powder which was soluble in ethanol and from which no pure compounds could be separated by repeated fractional reprecipitation. The analysis of this material (13.04% Si; 1.09% Zn) indicated that it might be a mixture of metallosiloxane polymer and hexaphenyltrisiloxane-1,5-diol (or other siloxanes).

Decomposition of polymers for analysis. The polymers were decomposed for analysis by the conventional wet-ashing technique using concentrated sulfuric and nitric acids.

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BATON ROUGE, LA.

[CONTRIBUTION FROM THE BIOMEDICAL RESEARCH GROUP OF THE LOS ALAMOS SCIENTIFIC LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Liquid Scintillators. VII. 2,5-Diaryl Substituted Thiazoles as Liquid Scintillator Solutes[1]

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A number of 2,5-diaryl substituted thiazoles have been evaluated as liquid scintillator solutes. A comparison of the effect of substituent groups upon the pulse height of the thiazoles has shown a marked improvement only with the 4-pyridyl and the *p*-dimethylaminophenyl groups. The thiazole pulse heights, fluorescence spectra, and ultraviolet absorption spectra have been compared with the analogous oxazoles.

In an effort to improve upon the existing liquid scintillator counting solutions and to provide data which would help to correlate chemical structure with the ability of various solutes to scintillate, a large number of organic compounds have been investigated.[2–4]

By and large, those solutes which contain sulfur are generally thought to scintillate with a low efficiency, if at all. Thus when Arnold[5] tested a substituted phenylbenzothiazole, it gave a wholly unexpected result. This compound, 2-(*p*-dimethylaminophenyl)benzothiazole, gave a pulse height which was 75% of that of the best solute which had been tested, whereas 2-phenylbenzothiazole was "dead."[6]

There were available in this laboratory a number of oxazole intermediates which could be readily converted to thiazoles. The products of these syntheses would give thiazoles which would have directly comparable oxazoles and thus could provide a comparison of the effects of substituent groups.

Table I contains the data for evaluation of the thiazoles; the maximum relative pulse height (I_{max}); the concentration of solute at I_{max} (c_{max}); the wave length of maximum emission and the mean wave length of the fluorescence spectra (λ^{fl}_{max} and $\bar{\lambda}$, respectively); and the ultraviolet absorption data (λ^{abs}_{max} and ϵ_{max}).

A comparison of the thiazole pulse heights with those of the corresponding oxazoles (in parentheses) shows that in no case does the thiazole equal or excel the oxazole. The highest pulse height obtained is only 80% of that of the analogous oxazole.

The importance of the effects produced by substitution has been noted by several authors.[6,7]

The effect of substitution can be measured relative to 2,5-diphenylthiazole, which can be regarded as the parent member of this series. Several groups produce very little change in the ability of the solute to scintillate. These are the *p*-chlorophenyl, *p*-fluorophenyl, 1-naphthyl, 3-pyridyl, and styryl groups. The 2-naphthyl and 4-biphenylyl groups

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[1] (a) Work performed under the auspices of the U. S. Atomic Energy Commission. (b) Paper VI: M. D. Barnett, G. H. Daub, F. N. Hayes, and D. G. Ott, *J. Am. Chem. Soc.*, **81**, 4583 (1959).

[2] F. N. Hayes, V. N. Kerr, D. G. Ott, E. Hansbury, and B. S. Rogers, Los Alamos Scientific Laboratory Report **LA-2176**, Office of Technical Services, U. S. Dept. Commerce, Washington 25, D. C. (1958).

[3] H. Kallman and M. Furst, *Phys. Rev.*, **79**, 857 (1950).

[4] H. Kallman and M. Furst, *Nucleonics*, **13**, No. 3, 32 (1951).

[5] J. R. Arnold, *Science*, **122**, 1139 (1955).

[6] F. N. Hayes, D. G. Ott, V. N. Kerr, and B. S. Rogers, *Nucleonics*, **13**, No. 12, 38 (1955).

[7] H. Gilman, E. A. Weipert, T. Soddy, and F. N. Hayes, *J. Org. Chem.*, **22**, 1169 (1957).