## **1135.** *A Study of Hydrogen Bonding in Poly(diorganosiloxane)-αω-diols.*

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The preparation of poly(dimethyl- and diphenyl-siloxane)-αω-diols is described, together with an infrared examination of their hydrogen bonding. Both intramolecular and intermolecular hydrogen bonding have been found in hexaphenyl- and hexamethyl-trisiloxane-1,3-diol and longer-chain poly(dimethylsiloxane)-αω-diols. The relative acidities and basicities of these diols, as measured by the frequency shifts on hydrogen bonding with diethyl ether and phenol, are reported and their theoretical significance is discussed.

In view of the importance of dichlorodimethylsilane in the silicone industry, it is surprising that only the first two members of the diol series, $HO{\cdot}[Me_2Si{\cdot}O]_n{\cdot}H$ derivable from this compound have been reported. This has been due to the marked tendency of these silanols to condense in acidic or alkaline conditions. The first direct synthesis of dimethylsilanediol[1] required hydrolysis of dichlorodimethylsilane in an aqueous solution of aluminium sulphate containing magnesium carbonate, while hydrolysis in water, kept nearly neutral by ammonia gas, yielded tetramethyldisiloxane-1,3-diol.[2] A general procedure for preparing these two diols, in addition to hexamethyltrisiloxane-1,5-diol, octamethyltetrasiloxane-1,7-diol, and decamethylpentasiloxane-1,9-diol, has been developed, ammonium carbonate being used as the neutralising agent. The isolation of tetraphenyldisiloxane-1,3-diol and hexaphenyltrisiloxane-1,5-diol in poor yield on hydrolysis of dichlorodiphenylsilane with cold water has been reported,[3] as has their preparation through the corresponding αω-dichlorosiloxanes.[4] Our procedure has now afforded also the first three members of the diphenyl series.

The only published infrared data[5] on a homologous series of silicon-containing diols dealt with the first three members of the diphenyl series, in the solid state and carbon tetrachloride solution, the absorption bands attributable to free and associated hydroxyl vibrations being recorded.

Our objective was to examine the hydrogen bonding in poly(diorganosiloxane)-αω-diols and their relative proton-donating (acidity) and proton-accepting powers (basicity) by Kuhn's infrared procedure.[6] This involves measuring the hydroxyl-frequency shift

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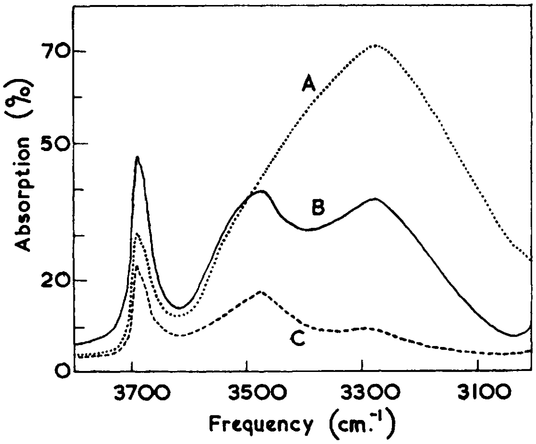
[1] Fukukawa and Kohama, *Sci. and Ind., Japan*, 1954, **28**, 261.
[2] Lucas and Martin, *J. Amer. Chem. Soc.*, 1952, **74**, 5225.
[3] Kipping, *J.*, 1912, **101**, 2125.
[4] Burkhard, *J. Amer. Chem. Soc.*, 1945, **67**, 2173.
[5] Richards and Thompson, *J.*, 1949, 124.
[6] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492.

produced by the interaction of a silanol and a reference acid or base, in this investigation, phenol and diethyl ether.

## Results and Discussion

Our method for the preparation of the eight diols has the advantage over previous procedures of simplicity and versatility. In the presence of an excess of water the pH value of the system remains in the range 8—6 throughout the hydrolysis, while the use of smaller amounts of water permits the system to become slightly acidic for limited periods and provides a novel method of preparing higher diols.

Tetramethyldisiloxane-1,3-diol and higher poly(dimethylsiloxane)-αω-diols in a high state of purity can be stored in Polythene containers in an undiluted state, but it is necessary to keep dimethylsilanediol as a suspension in pentane, preferably at 0°.



Infrared spectra of hexamethyltrisiloxane-1,5-diol in carbon tetrachloride: (A) 0·03M (1 mm. cells); (B) 0·003M (1 cm. cells); (C) 0·001M (1 cm. cells).

The annexed Table lists the frequencies of the free hydroxyl bands of the silanols in carbon tetrachloride, the frequency shifts (Δν) on association in a thin film and in solution, and the frequency shifts on reaction of the silanols with phenol and diethyl ether. The Figure gives a typical example of the change in the absorption bands of trisiloxane-1,5-diols and higher members with increasing dilution.

Infrared data.

| | | Frequency shifts | | | | |
|---|---|---|---|---|---|---|
| | | Intramol. bonding | Intermol. bonding | | | |
| Siloxane-αω-diols | Free OH | 0·003M | Film | 0·03M | Phenol–silanol | Silanol–ether |
| [$Me_2Si(OH)_2$] ............... | 3686 | — | 550 | — | — | 273 |
| Tetramethyldi ............ | 3686 | — | 481 | 402 | 268 | 275 |
| Hexamethyltri ............ | 3686 | 203 | 400 | 403 | 291 | 274 |
| Octamethyltetra ......... | 3686 | 203 | 401 | 406 | 291 | 273 |
| Decamethylpenta ......... | 3686 | 203 | 404 | 406 | 230 * | 270 |
| [$Ph_2Si(OH)_2$] ............... | 3674 | — | 469 | — | — | 329 |
| Tetraphenyldi ............ | 3674 | — | 425 | 284 | 190 | 328 |
| Hexaphenyltri ............ | 3674 | 210 | 380 | 384 | 243 | 325 |

* Δν ± 20 cm.$^{-1}$; others ±5 cm.$^{-1}$.

Bands due to intramolecular hydrogen bonding are given by the tri-, tetra-, and penta-siloxane-αω-diol of the dimethyl series and by hexaphenyltrisiloxane-1,5-diol. These bands, in the range 3490—3460 cm.$^{-1}$, are characterised by the retention of their intensity relative to the free hydroxyl bands on dilution. It is significant that intramolecular hydrogen bonding first appears in the trisiloxane-1,5-diol of both series and the lowest-membered cyclic siloxanes are the trimers. These facts suggest that intramolecular hydrogen bonding may be an important initial step in the formation of cyclosiloxanes.

Badger [7] established a relation between the energy of a hydrogen bond and the shift in frequency of the hydroxyl bands which accompanies the formation of the bond; the stronger the bond the greater is the shift. The strength of an intramolecular hydrogen bond will vary with the size of the ring being formed and should remain fairly constant once the number of ring atoms is sufficient to give a strain-free ring. For example, the shifts for intramolecular hydrogen bonding in a series of poly(methylene glycols) are ethylene glycol (32 cm.$^{-1}$), propane-1,3-diol (68 cm.$^{-1}$), and butane-1,4-diol (156 cm.$^{-1}$). By contrast, the chelate rings formed by the third, fourth, and fifth members of the poly(dimethylsiloxane)-αω-diol series appear to be strain-free, as $\Delta\nu$ is almost constant, and this is in accord with the known data on cyclic tri-, tetra-, and penta-siloxane. These three cyclic siloxanes have, of course, smaller-membered rings than the chelate rings produced by the diols and are consequently expected to be more strained. The estimated [8] strain energy of hexamethylcyclotrisiloxane is 3—4 kcal./mole, which indicates that even in the cyclic trimer, which has been shown [9,10] to be planar, there is very little strain. Further, there should be no increase in octamethylcyclotetrasiloxane and higher-membered cyclosiloxanes, which are puckered.[9,11]

The intramolecular hydrogen bonding in hexaphenyltrisiloxane-1,5-diol (210 cm.$^{-1}$) is slightly stronger than in hexamethyltrisiloxane-1,5-diol (203 cm.$^{-1}$).

Where the diols are sufficiently soluble in carbon tetrachloride two sets of frequency shifts due to intermolecular hydrogen bonding are given in the Table, for the 0·03M-solutions and the films. The pairs of values differ in some instances and this is generally recognised as being due to the more extensive association normally occurring with hydroxylated compounds in the undiluted state. The fact that $\Delta\nu$ for trisiloxane-1,5-diols in the solution and the film are equal indicates only limited interaction in the film. The reason probably lies with the manner in which simple diorganosilanediols interact [12] to produce chains and, in turn, sheets which form a layer structure with the organic substituents of neighbouring sheets contacting back to back. It seems likely that the degree of interaction would decrease as the siloxane chains increases, and the present results suggest that the association is limited to the formation of simple chains in the trisiloxane-1,5-diols and higher poly(diorganosiloxane)-αω-diols.

Several investigators [13] have established a correlation between $\Delta\nu$ and chemical reactivities. Application of this relationship to the values given in the Table for the diol films suggests a fall in reactivity over the first three members, before a constant level is attained. This accords with our knowledge of diol stability. The values for the 0·03M-solutions of diols are incomplete, but they indicate that at this dilution a constant level of reactivity has been reached in the dimethyl series with the disiloxane. The lower $\Delta\nu$ for tetraphenyldisiloxane-1,3-diol than for hexaphenyltrisiloxane-1,5-diol in solution must be due to some other factor.

The relative basicities of the diols were determined by examining solutions with the more powerful proton donor, phenol, and measuring the shift of the hydrogenic stretching frequency of the phenol. The large shifts must be due to hydrogen bonding between the hydroxyl groups of the diol and phenol, since the phenol shift due to the basicity of the

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[7] Badger, *J. Chem. Phys.*, 1940, **8**, 288.

[8] Piccoli, Haberland, and Merker, *J. Amer. Chem. Soc.*, 1960, **82**, 1883.

[9] Frevel and Hunter, *J. Amer. Chem. Soc.*, 1945, **67**, 2275.

[10] Aggarwal and Bauer, *J. Chem. Phys.*, 1950, **18**, 42.

[11] Frevel quoted by Flory, Mendelkern, Kinsinger, and Schultz, *J. Amer. Chem. Soc.*, 1952, **74**, 3364.

[12] Kukudo and Watase, *J. Chem. Phys.*, 1953, **21**, 167; Watase, Kasai, and Kakudo, *Ann. Rep. Text. Res. Inst. Osaka Univ.*, 1952, **6**, 38; Kakudo, Kasai, and Watase, *J. Chem. Phys.*, 1953, **21**, 1894.

[13] Gordy and Stanford, *J. Chem. Phys.*, 1940, **8**, 170; Ingraham, Corse, Bailey, and Stitt, *J. Amer. Chem. Soc.*, 1952, **74**, 2297.

siloxane-oxygen atoms generally falls in the range 137—147 cm.$^{-1}$.[14] The Δν in both series of diols suggest that there is an increase in basicity over the first three members, which is interpreted as being due to a decrease in the dative π-bonding from the hydroxyl-oxygen to silicon with the development of multi-centre π-bonding [14,15] in the siloxane chain.

The relative acidity of the diols was studied by measuring the shift of the hydroxyl stretching absorptions on hydrogen bonding to diethyl ether. In contrast to the basicity, the acidity of the dimethyl and diphenyl series of diols remains constant, giving values of about 273 and 327 cm.$^{-1}$, respectively, indicating that the protonic nature of the hydroxyl hydrogen is unaffected by the extensive π-bonding of the siloxane chain. The acidity is, however, increased in diols with phenyl groups bonded directly to silicon, a result in accord with that of another investigation.[16] This indicates that, in spite of π-bonding from the aromatic ring to silicon, the net effect of the presence of phenyl groups is electron-withdrawal.

## EXPERIMENTAL

In these preparations the strength of the commercial ammonium carbonate ($NH_4HCO_3,NH_2{\cdot}CO_2NH_4$) was established in terms of the neutralising power of ammonium carbonate immediately before use, and the necessary adjustments were made in the quantities employed.

*Dimethylsilanediol.*—Dichlorodimethylsilane (1 mole) was added dropwise, with stirring, at 0° in 2·5 hr., to an aqueous solution of ammonium carbonate (1·05 mole) containing sufficient water (46 mole) to give theoretically a 10% solution of dimethylsilanediol on completion of the hydrolysis. After being saturated with sodium chloride the aqueous solution was extracted repeatedly with diethyl ether, and the combined ethereal solutions were dried and evaporated in nitrogen under reduced pressure. The oily solid remaining was extracted with light petroleum (b. p. 40—60°), in which the oil was soluble, leaving the crude dimethylsilanediol. Recrystallisation from pentane–diethyl ether gave plates (38 g., 41%), m. p. 100·5° (Found: Si, 30·4; OH, 37·0. Calc. for $C_2H_8O_2Si$: Si, 30·5; OH, 36·9%).

The light petroleum extract yielded tetramethyldisiloxane-1,3-diol (3·5 g., 4·2%), m. p. 68·5°, and a polysiloxane fluid (5·0 g.) (Found: Si, 37·3; OH, 3·0%).

*Tetramethyldisiloxane*-1,3-*diol.*—Dichlorodimethylsilane (4 mole) was added in 2·5 hr. to ammonium carbonate (5·6 mole) in water (184 mole) as described above. The aqueous solution was saturated with sodium chloride and kept for 2 days at −5°, tetramethyldisiloxane-1,3-diol crystallising. This, when recrystallised from light petroleum (b. p. 40—60°), had m. p. 68·5° (129 g., 39%) (Found: Si, 33·5; OH, 20·4. Calc. for $C_4H_{14}O_3Si_2$: Si, 33·8; OH, 20·5%).

The fluid remaining on evaporation of the light petroleum filtrate was combined with that obtained from an ethereal extract of the aqueous solution, to yield after drying ($MgSO_4$) a colourless liquid (122 g.) (Found: Si, 34·1; OH, 9·7%).

*Hexamethyltrisiloxane*-1,5-*diol, Octamethyltetrasiloxane*-1,7-*diol, and Decamethylpentasiloxane*-1,9-*diol.*—Dichlorodimethylsilane (1 mole) was added in 2·5 hr. to diethyl ether (1160 ml.), water (2 mole), and ammonium carbonate (1·4 mole), as experiments described above, but the stirring period was continued after the addition until the pH was 6—7. The dried ethereal solution was evaporated in nitrogen under reduced pressure. The residue consisted of a colourless fluid (67 g.) and some tetramethyldisiloxane-1,3-diol (5 g., 6·0%), m. p. 68°.

The fluid (50 g.) gave three diols on fractionation through a 8-cm. Vigreux column in nitrogen under reduced pressure: hexamethyltrisiloxane-1,5-diol (16 g.), b. p. 72—74°/0·3 mm., $n_D^{25}$ 1·4050 (Found: C, 29·8; Si, 34·6; OH, 13·8. Calc. for $C_6H_{20}O_4Si_3$: C, 30·0; Si, 35·0; OH, 14·1%) (Pike [17] gives b. p. 89—91/3 mm., $n_D^{25}$ 1·4063—1·4067); *octamethyltetrasiloxane*-1,7-*diol* (5 g.) b. p. 86—88°/0·4 mm., $n_D^{25}$ 1·4066 (Found: C, 30·7; Si, 35·4; OH, 10·6. $C_8H_{26}O_5Si_4$ requires C, 30·5; Si, 35·7; OH, 10·8%); and *decamethylpentasiloxane*-1,9-*diol* (3 g.), b. p. 100·5°/0·5 mm., $n_D^{25}$ 1·4067 (Found: C, 30·7; Si, 35·8; OH, 8·9. $C_{10}H_{32}O_6Si_5$ requires C, 30·9; Si, 36·1; OH, 8·75%).

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[14] West, Whatley, and Lake, *J. Amer. Chem. Soc.*, 1961, **83**, 761.
[15] Craig, *J.*, 1959, 997.
[16] West and Baney, *J. Amer. Chem. Soc.*, 1959, **81**, 6145.
[17] Pike, *J. Polymer Sci.*, 1961, **50**, 151.

The same diols were obtained on fractionating the fluid formed when neat dimethylsilanediol condensed during storage at room temperature in a Polythene container.

*Diphenylsilanediol.*—Dichlorodiphenylsilane (1 mole), added to ammonium carbonate (1·4 mole), water (108 mole), and diethyl ether (2728 ml.) in 2·5 hr., as outlined above, yielded diphenylsilanediol, m. p. 165° (from benzene) (205 g., 95%) (Found: Si, 13·0; OH, 15·9. Calc. for $C_{12}H_{12}O_2Si$: Si, 13·0; OH, 15·7%).

*Tetraphenyldisiloxane*-1,3-*diol and Hexaphenyltrisiloxane*-1,5-*diol.*—Dichlorodiphenylsilane (1·5 mole) was added in 45 min. to ammonium carbonate (2·1 mole), diethyl ether (1365 ml.), and water (1·5 mole), stirred at room temperature. The mixture was then boiled under reflux for 12 hr., water (500 ml.) added, and the neutral ethereal phase dried and evaporated. Diphenylsilanediol (21 g., 6·4%), m. p. 162°, was isolated as the insoluble component on repeated extraction of the white residue with cold benzene. The evaporated benzene extract yielded a white solid which on fractional recrystallisation from benzene–light petroleum (b. p. 80—100°) gave tetraphenyldisiloxane-1,3-diol (160 g., 51%), m. p. 115° [Found: C, 69·6; Si, 13·5; OH, 8·3%; *M* (ebullioscopic in $CCl_4$; Ray's apparatus [18]), 405, 419, 426. Calc. for $C_{24}H_{22}O_3Si_2$: C, 69·5; Si, 13·5; OH, 8·2%; *M*, 415], and hexaphenyltrisiloxane-1,5-diol (55 g., 18%) m. p. 112° (Found: C, 70·4; Si, 14·0; OH, 5·7%; *M*, 616, 612. Calc. for $C_{36}H_{32}O_4Si_3$: C, 70·5; Si, 13·7; OH, 5·5%; *M*, 613).

*Anhydrous Chemicals.*—For the infrared investigation the carbon tetrachloride (spectroscopic grade) and diethyl ether were dried with phosphorus pentoxide and sodium, respectively, and fractionated immediately before use. "AnalaR" phenol was kept for 3 weeks in a desiccator over sulphuric acid. The silanols were stored in Polythene containers, the solids being dried over phosphorus pentoxide before use, while the analysis of the liquids was checked immediately before infrared examination.

*Infrared Spectra.*—Solution spectra in the 3-micron region were examined with a Unicam S.P. 700 double-beam spectrometer and the grating, with Infrasil cells of 1 cm. and 1 mm. path-length.

Solutions of the diols in carbon tetrachloride were examined at concentrations of 0·03M and 0·01M in the 1 mm. cells, and at 0·003M and 0·001M in the 1 cm. cells. The frequencies of the bands due to intermolecular hydrogen bonding were taken at 0·03M, although there was no significant change in these values at lower concentrations. The frequencies of the bands due to intramolecular hydrogen bonding were measured as soon as the degree of intermolecular association was sufficiently low for these bands to become well defined, generally at 0·003M.

The silanols were present at concentrations of 0·01M in carbon tetrachloride solutions of phenol and diethyl ether, a level at which the degree of intermolecular association is relatively low. The phenol was used at 0·04M- and the ether at 0·25M-concentration.

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[18] Ray, *Trans. Faraday Soc.*, 1952, **48**, 809.