# Studies on the Diamagnetic Susceptibility of Some Organic Derivatives of Silicon Containing Silicon–Oxygen Bonds

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**Abstract:** Diamagnetic susceptibilities of 21 organic derivatives of silicon containing Si–O bonds are reported. $\chi_{Si}$ in these compounds has been calculated either graphically or from Pascal's additivity rule, and the reasons for the variation of $\chi_{Si}$ have been discussed. $\chi_M$ of these silicon compounds has also been calculated theoretically from different wave-mechanical approaches.[1,2] A poor agreement has been obtained between the observed $\chi_M$ values and the corresponding values calculated according to Baudet and coworker's method, and this poor agreement has been analyzed in the light of different environmental conditions present in these molecules. An excellent agreement is obtained between experimental and calculated values from Hameka's method. $\chi_M$ values have been discussed and attributed to due considerations for the structural factors present in these silicon molecules which do contribute toward the molecular diamagnetism.

A survey of the literature[3] reveals that the silicon compounds containing Si–O bonds behave abnormally toward Si–O bond lengths, force constants, bond energies, and bond angle at O, etc., when compared to the analogous carbon compounds (containing C–O bonds). Diamagnetic behavior of silicon compounds may be considered quite interesting and important from the structural point of view. As no systematic study on the organic derivatives of silicon with regard to their molecular diamagnetism appears to have been made, the present investigation was undertaken with a view to extend experimental and theoretical diamagnetic studies and to analyze the results in the light of different structural factors which may be possible reasons for the abnormal behavior of silicon compounds.

## Experimental Section

Twenty-one silicon compounds containing Si–O bonds were prepared from the standard methods available in the literature.[4–8] The mass susceptibility of freshly prepared and distilled compounds was measured with a sensitive Gouy balance calibrated with a number of standard substances (conductivity water, dry benzene, naphthalene, nickel chloride solution, etc.) for more than 2 years in our laboratory. The solids were used in fine powdered form to eliminate the orientation effects, and the Gouy tube (fitted with ground-glass joints) was filled very carefully to ensure uniformity of packing. Utmost care was taken to exclude moisture in filling the Gouy tube as many of these silicon compounds are highly hydrolyzable. The measurement on each compound was performed a number of times (from five to eight). Reproducibility of the results was quite satisfactory. The average of the values differing only by ±0.5% has been taken. The Gouy force is of the order of ±0.05 mg. The Gouy tube was hung in such a manner that its one end remained in the center of the field and other out of the influence of the field, so that the susceptibility could be calculated by a well-established method.[9,10] Mass susceptibility has been converted into molecular susceptibility by multiplyng it with the molecular weight of the compound. The values are summarized in Table I.

## Discussion

A plot of $\chi_M$ against $n$ for the dimethyldi-$n$-alkoxysilanes represented by $(CH_3)_2Si[O(CH_2)_nH]_2$ has been plotted, and a linear graph was obtained showing that the additivity rule is followed in this series. The ordinate intercept for this plot was 58.50 which represents the mean susceptibility contribution of $(CH_3)_2Si[O(CH_2)_nH]_2$ when $n = 0$. Taking $\chi_H = 2.0$,[11] $\chi_O = 5.3$,[1] and $\chi_{CH_3} = 13.45$,[12] and using the additivity rule in the form

$$\chi_{(CH_3)_2Si[O(CH_2)_0H]_2} = 2\chi_{CH_3} + 2\chi_H + 2\chi_O + \chi_{Si} = 58.50$$

the mean $\chi_{Si}$ in this series has been calculated to be 17.00.

$\chi_M = 93.0$ (for $n = {}^3/_2$) and $\chi_M = 160$ (for $n = {}^9/_2$) are from the plot, and these values give $\chi_{CH_2} = 11.17$ which is in good agreement with that reported in the literature ($\chi_{CH_2} = 11.05$).[13]

The rest of the compounds dealt with in this paper do not form a homologous series and it is not possible to study them graphically; $\chi_{Si}$ in these compounds was obtained by subtracting $\chi_C = 7.40$;[14] $\chi_{CH_2} = 11.36$[15] and $\chi_{COO} = 15.15$[15] in addition to $\chi_H$, $\chi_{CH_3}$, and $\chi_O$ reported earlier. $\chi_{Si}$ values for these compounds have been summarized in Table I. $\chi_{Si}$'s in dimethyldiisopropoxysilane and dimethyldiisobutoxysilane are 18.00 and 17.91, respectively, and these values are higher than the average $\chi_{Si} = 17.00$ in the corresponding dimethyldi-$n$-alkoxysilanes. The higher value of $\chi_{Si}$ in an iso isomer than in the corresponding normal isomer may probably be due to the higher value of $\chi_M$

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(1) A. Pascal, J. Hoarau, and A. Marchand, *Advan. Chem. Phys.*, **3**, 171, 238 (1961).

(2) H. F. Hameka, *J. Chem. Phys.*, **34**, 1996 (1961).

(3) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, Oxford, 1963, p 124.

(4) R. C. Mehrotra and B. C. Pant, *J. Indian Chem. Soc.*, **39**, 65 (1962).

(5) B. C. Pant, Ph.D. Thesis, Rajasthan University, Jaipur, India, 1963: (a) pp 82–84; (b) p 100.

(6) R. C. Mehrotra and B. C. Pant, *J. Indian Chem. Soc.*, **41**, 563 (1964)

(7) R. C. Mehrotra and B. C. Pant, *Tetrahedron Letters*, **5**, 321 (1963).

(8) See ref 5, pp 96–124.

(9) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(10) R. R. Gupta, Ph.D. Thesis, Rajasthan University, Jaipur, India, 1968, p 40.

(11) W. Haberditzl, *Z. Chem.*, **1**, 255 (1961).

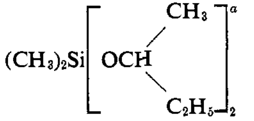
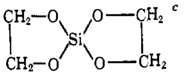
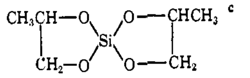
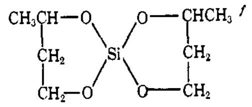
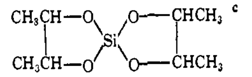
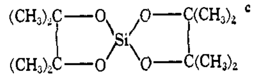
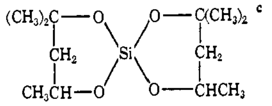
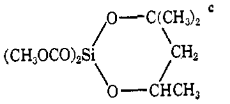
(12) W. R. Angus, G. I. W. Llewelyn, and G. Stott, *Trans. Faraday Soc.*, **55**, 837 (1959).

(13) E. W. Abel, R. P. Bush, C. R. Jenkins, and T. Zobel, *ibid.*, **60**, 1214 (1964).

(14) Ya. G. Dorfman, "Diamagnetism and the Chemical Bond," Edward Arnold (Publishers), Ltd., London, 1965, p 24.

(15) P. Pascal, A. Pacault, and J. Hoarau, *Compt. Rend.*, **223**, 1078 (1951).

**Table I**

| Compd no. | Name | Formula | $\chi_M$ | $\chi_M$ (others if any) | $\chi_{Si}$ |
|---|---|---|---|---|---|
| 1 | Dimethyldimethoxysilane | $(CH_3)_2Si(OCH_3)_2{}^a$ | 81.95 | 81.70[g]<br>81.60[h] | 17.00[k] |
| 2 | Dimethyldiethoxysilane | $(CH_3)_2Si(OC_2H_5)_2{}^b$ | 104.20 | 103.60[g]<br>104.70[i]<br>104.60[j] | 17.00[k] |
| 3 | Dimethyldi-*n*-propoxysilane | $(CH_3)_2Si[O(CH_2)_2CH_3]_2{}^a$ | 126.90 | 125.70[g] | 17.00[k] |
| 4 | Dimethyldiisopropoxysilane | $(CH_3)_2Si[OCH(CH_3)_2]_2{}^a$ | 128.10 | | 18.00 |
| 5 | Dimethyldi-*n*-butoxysilane | $(CH_3)_2Si[O(CH_2)_3CH_3]_2{}^a$ | 149.40 | 147.40[g] | 17.00[k] |
| 6 | Dimethyldiisobutoxysilane | $(CH_3)_2Si[OCH_2CHCH_3)_2]_2{}^b$ | 150.73 | | 17.91 |
| 7 | Dimethyldi-*sec*-butoxysilane |  $(CH_3)_2Si\left[OCH\begin{matrix}CH_3\\C_2H_5\end{matrix}\right]_2^a$ | 150.83 | | 18.01 |
| 8 | Dimethyldi-*n*-amyloxysilane | $(CH_3)_2Si[O(CH_2)_4CH_3]_2{}^a$ | 172.37 | | 17.00[k] |
| 9 | Ethanediol derivative of silicon |  [c] | 80.94 | | 14.50 |
| 10 | 1,2-Propanediol derivative of silicon |  [c] | 104.34 | | 14.72 |
| 11 | 1,3-Butanediol derivative of silicon |  [f] | 126.43 | | 14.09 |
| 12 | 2,3-Butanediol derivative of silicon |  [c] | 127.12 | | 14.52 |
| 13 | Pinacol derivative of silicon |  [c] | 172.48 | | 14.08 |
| 14 | Hexylene glycol derivative of silicon |  [c] | 172.27 | | 14.05 |
| 15 | Diacetoxyhexylene glycol derivative of silicon |  [c] | 150.65 | | 14.34 |
| 16 | Silicon tetraacetate | $Si(OCOCH_3)_4{}^d$ | 129.26 | | 14.86 |
| 17 | Silicon tetrapropionate | $Si(OCOC_2H_5)_4{}^e$ | 173.85 | | 14.00 |
| 18 | Dimethyldiacetoxysilane | $(CH_3)_2Si(OCOCH_3)_2{}^f$ | 101.18 | | 17.08 |
| 19 | Dimethyldipropionoxysilane | $(CH_3)_2Si(OCOC_2H_5)_2{}^f$ | 123.97 | | 17.15 |
| 20 | Trimethylacetoxysilane | $(CH_3)_3Si(OCOCH_3){}^f$ | 86.99 | | 18.06 |
| 21 | Trimethylpropionoxysilane | $(CH_3)_3Si(OCOC_2H_5){}^f$ | 99.09 | | 18.78 |

[a] Reference 4. [b] Reference 5a. [c] Reference 6. [d] Reference 7. [e] Reference 5b. [f] Reference 8. [g] E. W. Abel, R. P. Bush, C. R. Jenkins, and T. Zobel, *Trans. Faraday Soc.*, **60,** 1214 (1964). [h] R. L. Mital, *Bull. Chem. Soc. Japan*, **37,** 1440 (1964). [i] R. L. Mital, *J. Phys. Chem.*, **68,** 1613 (1964). [j] R. M. Mathur, *Trans. Faraday Soc.*, **54,** 1477 (1958). [k] Average value of $\chi_{Si}$ determined from the plot of $\chi_M$ against *n* in the series $(CH_3)_2Si[O(CH_2)_nH]_2$. All the susceptibility values are in cgs units $\times 10^{-6}$ (throughout the paper).

of the iso isomer than that of the normal isomer. It is remarkable to note that in these organic derivatives of silicon the iso isomer is more diamagnetic than the normal isomer and forms an analogous case to the different series of organic compounds.[16-20]

$\chi_{Si}$ values in dimethyldiacetoxy- and dimethyldipropionoxysilanes are 17.08 and 17.15, respectively, giving an average of $\chi_{Si}$ = 17.12. $\chi_{Si}$ in the glycol derivatives ranges from 14.05 to 14.72 giving an average of 14.33. In silicon tetraacetate and tetrapropionate $\chi_{Si}$'s are 14.86 and 14.00, respectively, and correspond to an average value of $\chi_{Si}$ = 14.43 which is very near to $\chi_{Si}$ = 14.33 (in the glycols derivatives). In trimethylacetoxy- and -propionoxysilanes $\chi_{Si}$'s are 18.06 and 18.78, respectively, and for these two compounds the average $\chi_{Si}$ = 18.42.

On the basis of the diamagnetism of atomic silicon, these silicon compounds can be classified as shown in Table II. This observation shows that $\chi_{Si}$ is nearly constant in the compounds containing the same number of Si–O bonds, and it changes considerably as the number of Si–O bonds varies. $\chi_{Si}$ decreases as the number of Si–O bonds increases. The value of $\chi_{Si}$ is minimum when the number of Si–O bonds (four) is maximum. This observation permits us to conclude

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(16) P. W. Selwood, "Magneto-Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1955 p 95.

(17) W. R. Angus, G. I. W. Llewelyn, and G. Stott, *Trans. Faraday Soc.*, **51**, 241 (1955).

(18) S. S. Bhatnagar and K. N. Mathur, "Physical Principles and Applications of Magneto-Chemistry," Macmillan and Co. Ltd., London, 1935, p 139.

(19) R. R. Gupta and R. L. Mital, *Ann. Soc. Bruxelles*, **81**, 183 (1967).

(20) W. R. Angus and W. K. Hill, *Trans. Faraday Soc.*, **39**, 197 (1943).

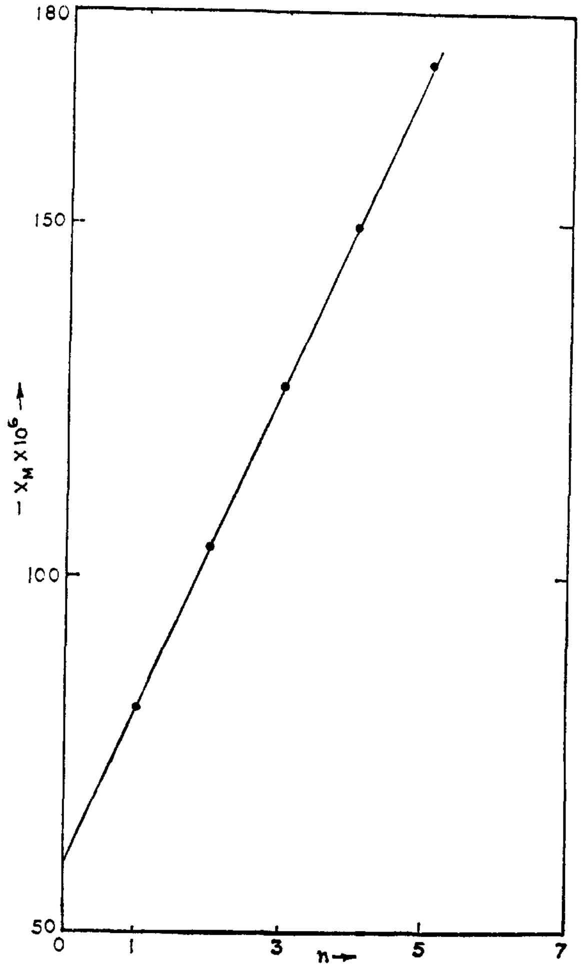

Figure 1. Plot of $\chi_M$ *vs.* *n* in the series $(CH_3)_2Si_n(OCH_2)_nH]_2$.

that there is something fundamental involved with Si–O bond and gives rise to depression in $\chi_{Si}$ when a Si–C bond is replaced by a Si–O bond. When all the four bonds are Si–C bonds, $\chi_{Si}$ is much higher ($\chi_{Si} = 21.0$).[13]

**Table II**

| Compounds | No. of Si–O bonds | $\chi_{Si}$ (average) |
|---|---|---|
| Trimethylacetoxy- and trimethylpropionoxysilanes | 1 | 18.42 |
| Dimethyldialkoxysilanes | 2 | 17.00 |
| Dimethyldiacetoxy- and dimethyldipropionoxysilanes | 2 | 17.11 |
| Glycol derivatives of silicon | 4 | 14.33 |
| Tetraacetoxy- and tetrapropionoxysilanes | 4 | 14.43 |

In these organic derivatives of silicon, the central Si atom is attached to the oxygen atom (or atoms) having lone pairs of electrons, and therefore, the $p_\pi$–$d_\pi$ bonding results between the silicon atom and the lone pairs of electrons. Although oxygen atom has two lone pairs of electrons, only one of these can be involved with any one silicon atom.[21] The formation of $p_\pi$–$d_\pi$ bonding suggests that the lone pair of electrons on oxygen interacts with vacant d orbitals of the silicon atom, and this implies that the d orbital of silicon atom has sufficiently contracted to become of energy and spatial extent appropriate for mixing with the s and p orbitals. These $p_\pi$–$d_\pi$ interactions have been discussed in detail by Ebsworth.[22] In this state of affairs, there should be a drop in $\Sigma\bar{r}^2$ in these molecules, and this drop in $\Sigma\bar{r}^2$ brings about a depression in Pauli's diamagnetic term in the well-known Van Vleck quantum-mechanical equation given below

$$\chi_M = \frac{-Ne^2}{6mc^2}\sum \bar{r}^2 + \frac{2}{3}\sum_{n \neq n}\frac{|m_0(n,n')|^2}{h\nu(n',n)}$$

The over-all effect of such $p_\pi$–$d_\pi$ bonds caused by the interactions of the lone pairs on oxygen with d orbitals of silicon results in lowering of the $\chi_{Si}$ value. The resultant lowering in $\chi_{Si}$ depends on the number of Si–O bonds in the molecules, and it may be expected that the greater the number of Si–O bonds in the molecule, the greater is the decrease in $\chi_{Si}$. This explanation strongly supports our experimental results. There is much controversy over the atomic susceptibility of silicon; values ranging from $\chi_{Si} = 21.0$[13] to $-3.01$[23] have been reported. The above discussion will be of help in this direction in explaining this abnormality.

## Calculation of Molecular Susceptibility

A wave-mechanical scheme for calculating the molecular susceptibility, developed theoretically by Baudet and coworkers,[24,25] has been used to calculate the susceptibility of these silicon derivatives. In this scheme, the molecular susceptibility is treated as a bond property instead of an atomic property, and it is considered that the molecular susceptibility is contributed by the following types of electrons present in the atoms constituting the molecule: (a) bonding electrons, *i.e.*, the electrons which form the bonds in the molecule (BE); (b) nonbonding electrons in outer shells, *i.e.*, the electrons which are not participating in the bond formation (NBE); (c) electrons of inner shells of each atom (ISE); and (d) $\pi$ electrons present in each $\pi$ bond.

This scheme permits us to express the molecular susceptibility of a compound as

$$\chi_{M(\text{theoretical})} = \sum\chi_{BE} + \sum\chi_{NBE} + \sum\chi_{ISE} + \sum\chi_{\pi\ \text{electron}}$$

Diamagnetic contributions toward molecular susceptibility due to these different types of electrons in a number of bonds and atoms have been calculated wave mechanically by Baudet and coworkers,[24,25] and these values[1] have been used to calculate $\chi_M$ values of silicon compounds. These calculated $\chi_M$ values have been summarized in Table III.

The percentage deviation in the dimethyldialkoxysilanes ranges from $-1.7$ to $-4.2$ and is a maximum for dimethyldimethoxysilane. A critical examination of these percentage deviations shows that the percentage deviation decreases as the number of carbon atoms in the alkoxy group increases with the increase in their molecular weight and molecular diamagnetism. This observation indicates that the factor which may be considered responsible for the

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(21) R. West and R. H. Baney, *J. Am. Chem. Soc.*, **81**, 6145 (1959).

(22) See ref 3.

(23) R. M. Mathur, *Trans. Faraday Soc.*, **54**, 1477 (1958).

(24) J. Baudet, *J. Chim. Phys.*, **58**, 228 (1961).

(25) J. Baudet, J. Tillieu, and J. Guy, *Compt. Rend.*, **244**, 2920 (1957).

**Table III.** Calculated $\chi_M$ Values

| Compd no. | Calculated wave mechanically[1] |  | Calculated from Hameka's equation[2] |  |
|---|---|---|---|---|
|  | $\chi_M$ | % $\Delta\chi_M$ | $\chi_M$ | % $\Delta\chi_M$ |
| 1 | 85.30 | −4.2 | 81.92 | +0.04 |
| 2 | 108.00 | −3.6 | 104.26 | −0.06 |
| 3 | 130.70 | −2.8 | 126.60 | +0.24 |
| 4 | 130.70 | −2.0 |  |  |
| 5 | 153.40 | −2.7 | 148.94 | +0.31 |
| 6 | 153.40 | −1.8 |  |  |
| 7 | 153.40 | −1.7 |  |  |
| 8 | 176.10 | −2.2 | 171.32 | +0.03 |
| 9 | 86.10 | −6.4 |  |  |
| 10 | 108.80 | −4.3 |  |  |
| 11 | 131.50 | −4.0 |  |  |
| 12 | 131.50 | −3.4 |  |  |
| 13 | 176.90 | −2.6 |  |  |
| 14 | 176.90 | −2.7 |  |  |
| 15 | 160.86 | −6.8 |  |  |
| 16 | 144.82 | −12.1 | 128.68 | +0.45 |
| 17 | 190.22 | −9.4 | 174.08 | −0.13 |
| 18 | 109.66 | −8.4 | 101.32 | −0.04 |
| 19 | 132.36 | −6.8 | 123.82 | +0.12 |
| 20 | 92.08 | −5.8 | 87.70 | −0.82 |
| 21 | 103.43 | −4.4 | 99.05 | +0.04 |

deviation may be common and may be contributing almost to the same extent in all the dimethyldialkoxysilanes. The sequence exists in the glycol derivatives (except in diacetoxyhexylene glycol derivative) of silicon, silicon tetraacetate and silicon tetrapropionate, dimethyldiacetoxy- and dimethyldipropionoxysilanes, and trimethylacetoxy- and trimethylpropionoxysilanes. The percentage deviation for silicon tetraacetate is 12.1 (very high) which is even of higher order than Tillieu's susceptibility data[26] which have a spread of as much as 10% even after using Coulson's wave-function parameters. Comparatively the percentage deviation for silicon tetraacetate is much more than for other compounds of silicon (excluding the compounds containing the acetoxy groups), and therefore it is not justified, in any case, to conclude that the factor which is responsible for the deviation in other compounds is the only factor causing deviation in the case of silicon tetraacetate; but in addition to this factor, there is something more which is causing such a big deviation for silicon tetraacetate and it cannot be ignored. It seems that the presence of the carbonyl group (C=O) in the vicinity of the oxygen atom (attached to silicon atom) is playing some role which is responsible for such a big deviation in silicon tetraacetate and a greater order deviation in the acetoxy compounds. It is quite remarkable and interesting to note the percentage deviation, −6.8, for the diacetoxyhexylene glycol derivative of silicon and the hexylene glycol derivative of silicon, −2.7. Both the compounds contain the same number of Si–O bonds, but the former differs from the latter in having acetoxy groups. The greater percentage deviation for the diacetoxyhexylene glycol derivative may be due to the presence of the linkage Si—O—C=O (*i.e.*, the presence of C=O in the vicinity of the oxygen atom bonded to the silicon atom).

The agreement between the wave-mechanically calculated and observed molecular susceptibilities is poor for these organic derivatives of silicon. Although the diamagnetic contribution from all type of sources toward molecular susceptibility have been duly considered, the environmental conditions, which cannot be neglected, have not been taken into these wave-mechanical calculations, and this is the reason that these calculations fail to give the different values for the positional isomers having different structures. It has been already pointed out that in these silicon compounds the action of $p_\pi$–$d_\pi$ bonding between the silicon atom and the lone pairs of electrons of oxygen is present, and this interaction has not been considered in these wave-mechanical calculations. This may be the probable cause for the difference in calculated and experimental $\chi_M$ values.

It may be inferred that this wave-mechanical scheme cannot be applied to calculate $\chi_M$ values of these organic derivatives of silicon with accuracy until and unless all the types of interactions are duly accounted for.

**Calculation of $\chi_M$ from Hameka's Wave-Mechanical Equation.**[2] For 11 silicon compounds $\chi_M$ has been calculated from Hameka's equation in which the molecular susceptibility of a compound is considered to be made up of (1) each atom, (2) each bond, and (3) each interaction between any two bonds starting from the same atom. Mathematically this equation can be represented by

$$\chi_M = \sum\chi(\text{atoms}) + \sum\chi(\text{bonds}) + \sum\chi(\text{bond interactions})$$

The sizes of the terms in this equation depend on the atoms involved. Hameka's equation for a compound of the formula $(CH_3)_aSi(OC_nH_{2n+1})_b$ can be expressed in the form

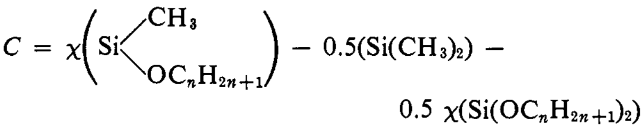
$$\chi_M = aA + bB + abC$$

where $A$, $B$, and $C$ are the parameters related to Hameka's various terms as explained below

$$A = 0.25\chi(Si) + \chi(CH_3) + \chi(SiCH_3) + 1.5(Si(CH_3)_2)$$

where $\chi(Si)$ and $\chi(CH_3)$ are the contributions of the silicon atom and the $CH_3$ group, and $(Si(CH_3)_2)$ is the term due to the interaction of two Si–$CH_3$ bonds to the same silicon atom. Similarly for other terms

$$B = 0.25\chi(Si) + \chi(OC_nH_{2n+1}) + \chi(SiOC_nH_{2n+1}) + 1.5\chi(Si(OC_nH_{2n+1})_2)$$



$$C = \chi\left(Si\begin{matrix}CH_3\\OC_nH_{2n+1}\end{matrix}\right) - 0.5(Si(CH_3)_2) - 0.5\,\chi(Si(OC_nH_{2n+1})_2)$$

As regards the difference between methyl and ethyl compounds, the same treatment leads to the conclusion that there will be a certain increment in susceptibility on replacing a methyl group by an ethyl group, but no other parameter will be changed.

$\chi_M$ for $Si(CH_3)_4$ = 74.8, $\chi_M$ for $Si(C_2H_5)_4$ = 120.3, $\chi_M$ for $Si[(CH_2)_2CH_3]_4$ = 165.8, and $\chi_{CH_2}$ = 11.50[27] give $A$ = 18.58 units for methyl groups. $\chi_M$ for $Si(OCH_3)_4$ = 89.98[28] gives $B$ = 22.42. $\chi_M$ for $(CH_3)_2Si(OCH_3)_2$ =

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(26) See ref 14, p 10.

(27) M. W. Lister and R. Marson, *Can. J. Chem.*, **42**, 2101 (1964).

(28) Unpublished work.

81.95, $\chi_M$ for $(CH_3)_2Si(OC_2H_5)_2 = 104.20$, and $\chi_{CH_2} = 11.17$ gives $C = -0.02$.

Using these parameters, $\chi_M$ values for dimethyl di-*n*-alkoxysilanes have been calculated and summarized in Table III.

For $\chi_M$ values of acetoxy- and propionoxysilanes of the general formula $(CH_3)_aSi(OC{=}OC_nH_{2n+1})_d$, Hameka's equation has been used as

$$\chi_M = aA + dD + adE$$

where

$$D = 0.25\chi(\mathrm{Si}) + \chi(\mathrm{OCOC}_n\mathrm{H}_{2n+1}) + \chi(\mathrm{Si{-}OCOC}_n\mathrm{H}_{2n+1}) + 1.5\chi\left(\mathrm{Si}\begin{matrix}\diagup \mathrm{OCOC}_n\mathrm{H}_{2n+1}\\ \diagdown \mathrm{OCOC}_n\mathrm{H}_{2n+1}\end{matrix}\right)$$

and

$$E = \chi\left(\mathrm{Si}\begin{matrix}\diagup \mathrm{CH}_3\\ \diagdown \mathrm{OCOC}_n\mathrm{H}_{2n+1}\end{matrix}\right) - 0.5\chi\left(\mathrm{Si}\begin{matrix}\diagup \mathrm{OCOC}_n\mathrm{H}_{2n+1}\\ \diagdown \mathrm{OCOC}_n\mathrm{H}_{2n+1}\end{matrix}\right) - 0.5\chi\left(\mathrm{Si}\begin{matrix}\diagup \mathrm{CH}_3\\ \diagdown \mathrm{CH}_3\end{matrix}\right)$$

Substitution of $\chi_M$ for $Si(OCOCH_3)_4 = 129.26$, $\chi_M$ for $Si(OCOC_2H_5)_4$, and $\chi_{CH_2} = 11.35$ gives $D = 32.17$. $\chi_M$ for $(CH_3)_2Si(OCOCH_3)_2 = 101.18$ and $\chi_M$ for $(CH_3)_2Si(OCOC_2H_5)_2 = 123.97$ give $E = -0.08$. $\chi_M$ values calculated for acetoxy- and propionoxysilanes with these parameters have been recorded in Table III.

The agreement between the calculated and experimentally determined $\chi_M$ values is excellent and is very encouraging as the divergence is practically of the negligible order. This good agreement is due to the fact that in Hameka's equation the contribution of bond interactions has been fully accounted for which could not be taken in earlier wave-mechanical calculations.[1] No doubt since silicon is the larger atom, it would be expected that these interactions would be less, but they do occur. The environmental bond interactions do play an important role in the compounds containing Si–O bonds and this role affects diamagnetism considerably like other properties. The studies of these bond interactions open an entirely new field which is yet to be explored for the exact behavior of the organic derivatives of metals.

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# Kinetics of Metal Ion and Metal Chelate Catalyzed Oxidation of Ascorbic Acid. IV. Uranyl Ion Catalyzed Oxidation[1]

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**Abstract:** The kinetics of the uranyl ion catalyzed oxidation of ascorbic acid at 25 and 40° is reported. The dissociation constants of ascorbic acid at 40°, and at an ionic strength of 0.10 *M* ($KNO_3$), have been obtained from potentiometric titration data and are $2.69 \times 10^{-4}$ and $1.05 \times 10^{-12}$. The dissociation constants of ascorbic acid in $D_2O$ at 25° and at an ionic strength of 0.10 *M* ($KNO_3$) are $2.7 \times 10^{-5}$ and $6.00 \times 10^{-13}$. The uranyl ion catalyzed oxidation of ascorbic acid catalyzed by uranyl ion proceeds by a path first order with respect to substrate, catalyst, molecular oxygen, and hydrogen or deuterium ion concentrations, in accordance with the rate law, $k[H_2A][UO_2^{2+}]\cdot[H^+][O_2]$. The uranyl ion is less active as a catalyst than is the vanadyl ion. The deuterium isotope effect, $k_H/k_D$, for the uranyl ion catalyzed reaction was found to have the low value of 1.24. Activation parameters for the uranyl ion catalyzed oxidation are reported and compared with those of vanadyl ion catalyzed and uncatalyzed oxidations of ascorbic acid. A probable mechanism is proposed for the uranyl ion catalyzed reaction.

In an earlier paper[3] the kinetics of the catalysis of oxidation of ascorbic acid by the vanadyl ion, and by its aminopolycarboxylic acid chelates, was described. The present paper extends this work to uranyl ion catalysis. The kinetics and mechanism of metal ion catalysis in the oxidation of ascorbic acid have been the subject matter of several studies,[4-9] most of which were concerned with catalysis by copper(II) ion. The present work was undertaken as part of a general study of the effect of oxo metal ions as catalysts in the oxidation of ascorbic acid, and for comparison with earlier work on catalysis by the oxovanadium(IV) ion.

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