Determination of Methyl and Phenyl Groups in Methyl-Phenyl-Siloxane Polymer by NMR Spectroscopy

By Tsutomu KUBOTA and Tsutomu TAKAMURA

(Received June 22, 1959)

Chemical applications of NMR spectroscopy have been developed rapidly during recent few years. Although many reports have been published on its application to the molecular structure investigation and to the qualitative analysis, quantitative analysis using the NMR method has scarcely been reported[1] at all.

It has already been known that under an appropriate experimental condition the peak area of the resonance spectrum is directly proportional to the number of resonating atoms irrespective of their chemical nature[2,3]. Since the peak area depends both on the volume of specimen inserted in an effective part of a high frequency coil and on whether or not the specimen is placed at the right position in the coil, a calibration must always be performed with the identical sample container if the outer reference method is adopted. If, however, a suitable inner reference is used instead of an outer one, such a disadvantage can be avoided; and in addition to this, the authors have a great advantage that no standard substance is required. The inner reference method is done by mixing a sample material homogeneously with a known amount of any substance which produces a resonance peak and by referring to the peak area produced by the substance as a standard.

Shoolery et al. have pointed out the usefulness of the method, but have not made the actual application[4]. Muller and Goldenson have used the peak area method for their kinetic study of phospher compound[5] and Shaw and Elsken have shown that the peak height of differential form of spectrum can be applied to the quantitative analysis[6], but their purposes seem not to be in the complete examination of the inner reference method.

It is the purpose of the present study to examine the inner reference method and to bring it to a practical use, in which determination of methyl and phenyl groups in methyl-phenyl-siloxane polymer has been carried out. The linear relationship between the peak area and proton concentration has been found to exist in a wide range of experimental conditions, the determination being made without difficulty. The analytical results were compared with those obtained from the infrared analysis and it was found that they were in good agreement within the experimental error.

Experimental

Materials.—Dioxane and benzene of commercial guaranteed reagents were used without further purification. Acetone was purified by drying a commercial guaranteed reagent with unhydrous calcium chloride and by distilling twice. Water was purified by distilling the de-ionized water. All of the organosiloxanes were those synthesized and purified in the Tsurumi Research Laboratory of Tokyo Shibaura Electric Co. The boiling or melting point ranges of siloxanes were within ±0.5°C.

Measurements.—Approximately 0.6 ml. of each sample was poured by means of a syringe into a glass tube of 5 mm. in outer diameter which then was sealed off. If necessary, a glass tube of 2 mm. in outer diameter containing pure water was sealed in the outer tube at the co-axial position. These sealed tubes were offered to measurements. Since according to a preliminary examination, there exists no difference between the proton chemical shift obtained by using a soft lead glass tube as a sample container and that obtained by using a borosilicate glass tube, soft lead glass tubes were used throughout this work becauce of the ease of sealing them.

Proton NMR spectra were recorded with a Japan Electron Optics Laboratory NMR Spectrometer Model JNM-3. The applied resonance frequency was 40 Mc, the field sweep width, 87.5 and 175 milligauss, the sweep rate being controlled to 5 to 10 milligauss per second. All the measurements were carried out in a room whose air temperature was regulated to 25±1°C.

---

[1] C. A. Reilly, *Anal. Chem.*, **30**, 839 (1958).

[2] N. F. Chamberlain, ibid., **31**, 56 (1959).

[3] R. B. Williams, *Ann. N. Y. Acad. Sci.*, **70**, 800 (1958).

[4] C. F. Callis, J. R. von Wazer and J. N. Shoolery, *Anal. Chem.*, **28**, 269 (1956).

[5] N. Muller and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 5182 (1956).

[6] T. M. Shaw and R. H. Elsken, *Anal. Chem.*, **27**, 1983 (1955).

The proton chemical shift described in δ value was calibrated as follows: The spectrum was recorded for pure acetone using pure water as a reference. The distance between the peaks due to acetone and water was measured from the center of the peaks, the field width corresponding to the distance being decided by using the δ value of acetone, $\delta=-0.334$, which was given by Allred and Rochow[7]. All the measurements were repeated ten times for one sample, the data being averaged. The proton chemical shift of the methyl group attached to the silicon atom was found to be $\delta=-0.49$ for hexamethylsiloxane and methyl-phenyl-siloxane polymer, and that of the phenyl group to be $\delta=+0.22$ for cyclooctaphenyltetrasiloxane and methyl-phenyl-siloxane polymer.

The infrared spectrum was recorded with an automatic recording spectrometer which was specially designed by Professor H. Yoshinaga of Osaka University. Measurements were carried out with the carbon disulfide solutions of sample at various concentrations and by means of a rock salt cell of 0.1 mm. optical path length for quantitative use. The key bands taken for methyl and phenyl groups were the absorption bands at wave numbers of 2970 and 3030 cm^{-1}, respectively.

Results and Discussion

Prior to the quantitative determination on methyl-phenyl-siloxane polymer, calibration curves were drawn with some standard substances to ascertain that the proportionality really exists between a peak area due to methyl or phenyl group and the number of protons contained in the group. Hexamethylsiloxane and cyclooctaphenyltetrasiloxane were chosen as standards, because the chemical constitution of these substances is similar to that of the siloxane polymer. Although the most favorable case would be one where these substances could be mixed homogeneously at various mixing ratios, the solid of phenyl siloxane is only slightly soluble in methyl siloxane; therefore, benzene and dioxane were used as auxiliary standards. The peak area was measured by varying the mixing ratio for three binary systems, namely, hexamethylsiloxane-benzene, cyclooctaphenyltetrasiloxane-dioxane and benzene-dioxane, where each characteristic peak is well separated. The examples of spectra are shown in Fig. 1.

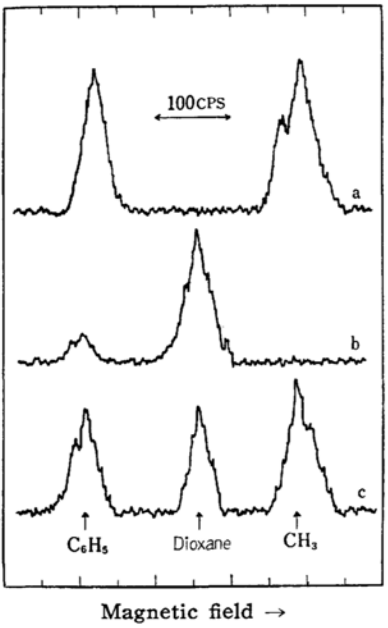

Fig. 1. Proton spin resonance spectra of binary mixtures containing organosiloxanes recorded at 40 Mc. and 25°C.
a) 46.1 weight % of hexamethylsiloxane in benzene;
b) 20.0% of cyclooctaphenyltetrasiloxane in dioxane;
c) 84.1% of methyl-phenyl-siloxane polymer in dioxane.

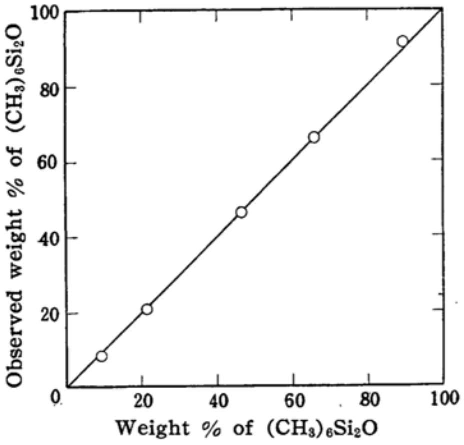

Fig. 2. Plotting of concentration of hexamethylsiloxane in benzene obtained from NMR spectra against that obtained from the mixing ratio.

In the case of the hexamethylsiloxane-benzene system two peaks appeared; the one is due to proton of benzene and the other to that of siloxane. The concentration of siloxane was obtained from the experimental results by taking the ratio of the peak area of benzene to that of siloxane and by multiplying the ratio by

---

[7] A. L. Allred and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 5361 (1957).

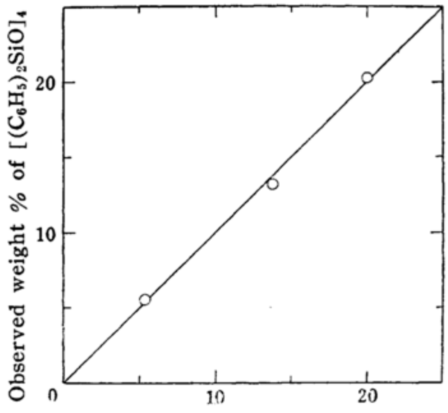

Fig. 3. Plotting of concentration of cyclooctaphenyltetrasiloxane in dioxane obtained from NMR spectra against that obtained from the mixing ratio.

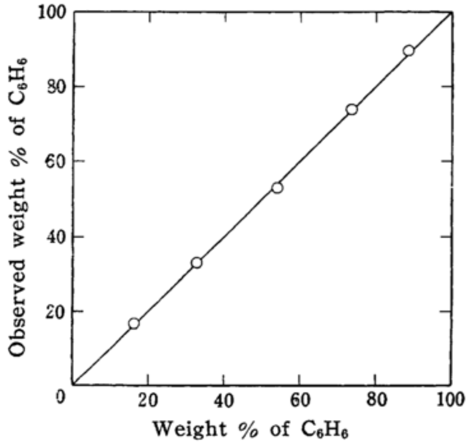

Fig. 4. Plotting of concentration of benzene in dioxane obtained from NMR spectra against that obtained from the mixing ratio.

a factor of 1/2, since benzene and siloxane molecules have six and twelve equivalent hydrogen atoms, respectively. The concentration of siloxane thus obtained was plotted against that determined by the mixing ratio. As seen in Fig. 2, the plots are well on the straight line whose slope is unity, the direct proportionality being confirmed. Similar plottings made on cyclooctaphenyltetrasiloxane-dioxane and benzene-dioxane systems gave also straight lines, the proportionality being ascertained as shown in Figs. 3 and 4. With the results of these experiments parallelly performed the direct proportionality was proved to be maintained in the mixture of hexamethylsiloxane and cyclooctaphenyltetrasiloxane.

The fact that the chemical shift of any respective group shows no difference whether the group is attached to simple siloxane or siloxane polymer shows these compounds to be nearly identical regarding the chemical construction. Therefore, the proportionality is supposed to be maintained also in the case of siloxane polymer.

Since the peak area measured at a definite recording condition depends on the sample volume located in the high frequency coil effectively, as already mentioned, the absolute number of protons can hardly be determined when outer reference is used. Such a difficulty is eliminated by mixing a known amount of a substance having proton with the sample homogeneously. Dioxane was chosen as a suitable reference. The actual measurement was made on the mixture of methylphenylsiloxane polymer and dioxane by varying the mixing ratio. Three well separated peaks appeared in this case as shown in Fig. 1, two from methyl and phenyl groups of siloxane polymer and one from dioxane. The peak area due to one proton can be obtained from the observed area of dioxane whose concentration is known, then, the numbers of methyl and phenyl groups involved in 100 g. of siloxane polymer can be calculated for each mixing ratio from the peak areas. The obtained values are listed in the second and fourth columns in Table I to show the constant value over a wide range of mixing ratio.

On the other hand, the number of each group was also determined with the infrared technique. Cyclooctamethyltetrasiloxane and cyclooctaphenyltetrasiloxane were used as standard substances for methyl and phenyl groups, respectively. Assuming that each extinction coefficient of a respective group in siloxane polymer is identical with that of the corresponding standard substance, the number was

TABLE I. NUMBERS OF METHYL AND PHENYL GROUPS PER 100 g. OF METHYL-PHENYL-SILOXANE POLYMER DETERMINED BY NMR AND INFRARED METHOD

Weight % of methyl-phenyl-siloxane polymer in dioxane	Number of methyl group		Number of phenyl group	
	NMR	Infrared	NMR	Infrared
84.1	1.21	—	0.56	—
54.5	1.16	—	0.55	—
44.0	1.14	—	0.57	—
30.1	1.15	—	0.56	—
mean	1.17	1.21	0.56	0.56

determined from the absorptions in carbon disulfide solution of known concentrations. The results averaged are cited in the third and fifth columns of Table I. Agreement of these results obtained from the two different methods is good within the experimental error.

The great advantage of NMR spectroscopy on the quantitative analysis is that no standard to the respective specimen is required because the peak area depends only on the number of protons and, under an appropriate experimental condition, is independent of the nature of molecular configuration. A comparatively large experimental error in the method caused by the crude reproducibility of the spectrum is now being reduced by the rapid development of instrumentation. The group type analysis on the relatively complicated molecule will then be systematized with the accumulation of chemical shift data, each number of atoms having nuclear spin would be determined for each group with the inner reference method, and therefore, the NMR method will display more power in the determination of molecular structure.

Summary

Proton spin resonance spectra were recorded for the three binary mixtures, benzene-dioxane, benzene-hexamethylsiloxane and dioxane-cyclooctaphenyltetrasiloxane whose mixing ratios were varied. The peak area due to resonating proton of methyl or phenyl group was found to be directly proportional for all systems to the number of protons which give the peak of respective groups over a wide range of recording conditions.

With the results obtained, the determination of methyl and phenyl groups in methyl-phenyl-siloxane polymer was carried out by the use of the inner reference method using dioxane. Siloxane polymer was mixed with dioxane and the spectrum was recorded for the mixture, the number of each group being calculated from the obtained peak area. The results were compared with those obtained from the infrared analysis and they were in good agreement within the experimental error.

The authors express their thanks to Dr. T. Harada, the Manager of Matsuda Research Laboratory, for his permission to publish this paper, to Dr. H. Miyazawa for his advice on the measurement of the NMR spectra and Mr. K. Kawazumi for the preparation and purification of organosilicon compounds.

Matsuda Research Laboratory
Tokyo Shibaura Electric Co.
Kawasaki