Thermochimica Acta, 13 (1975) 100–104

Note

Thermal stability of chlorinated dimethylpolysiloxanes

JOSÉ M. SOSA

Centro de Petróleo y Química, Instituto Venezolano de Investigaciones Científicas, Apartado 1827, Caracas 101 (Venezuela)

(Received 21 April 1975)

Polysiloxanes, commonly known as silicones, are generally considered very stable and chemically inert materials[1]. Recently, the reactivity of a silicone fluid with chlorine was tested after two serious explosions were traced to failure of materials widely used in chlorine service equipment[2]. This study revealed that silicone oil reacts violently with chlorine at temperatures as low as 88 °C. While the reactions of diphenyl- and dimethylpolysiloxanes with chlorine have been studied[3], the thermal stability of chlorinated siloxanes has not been evaluated extensively.

In our laboratory, a silicone oil of the DC 200 type was used inadvertently as a lubricant in a glass stirring mechanism employed in chlorination reactions. A white rubbery material was isolated from the stalled stirrer after it had been in contact with Cl_2 gas at atmospheric pressure for three hours.

Controlled chlorination reactions of a DC 200 silicone oil were undertaken and the resulting products were characterized. The thermal stability of the chlorinated products was evaluated under a nitrogen atmosphere.

In this report, the thermal stability of chlorinated silicone oils containing 15, 30 and 40% Cl by weight is compared to that of the parent DC 200 fluid.

EXPERIMENTAL

A silicone oil of the DC 200 type (360 cp at 20 °C) was chlorinated in a way similar to the one employed by Rotenberg[4] for normal paraffins. The method consists essentially of passing dry chlorine gas through the material at room temperature. In a typical reaction, chlorine gas is bubbled through 25 g of the oil at 200 cc min^{-1} starting at room temperature. After a short induction period, the temperature rises to 50 °C. The reaction is allowed to proceed until the oil becomes a sticky material. Twenty-five ml of CCl_4 are then added and the reaction is allowed to proceed until the desired chlorine content is obtained. Residual HCl and Cl_2 are removed from the product when the CCl_4 is distilled under vacuum.

The amount of chlorine in the samples was determined by obtaining the increase in weight of the starting material and by Schöniger's combustion method[5]. The amount of chlorine can also be estimated from the NMR spectra of the samples. Samples A, B and C contain 15, 30 and 40% Cl by weight, respectively.

IR spectra of the samples were obtained with a Perkin-Elmer Model 577 spectrometer as films between NaCl plates. NMR spectra were obtained on a Varian A-60 spectrometer in CCl_4.

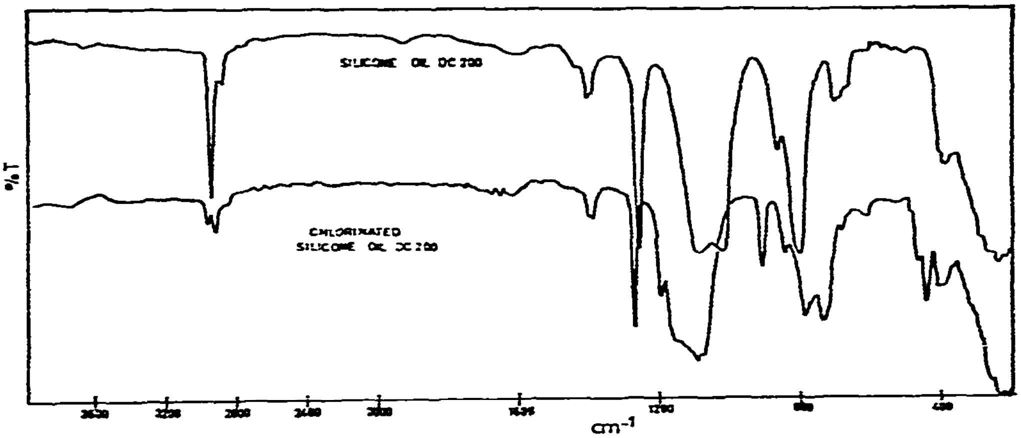


Fig. 1. IR spectra of Silicone DC 200 and of a chlorinated silicone oil containing 15% Cl by weight.

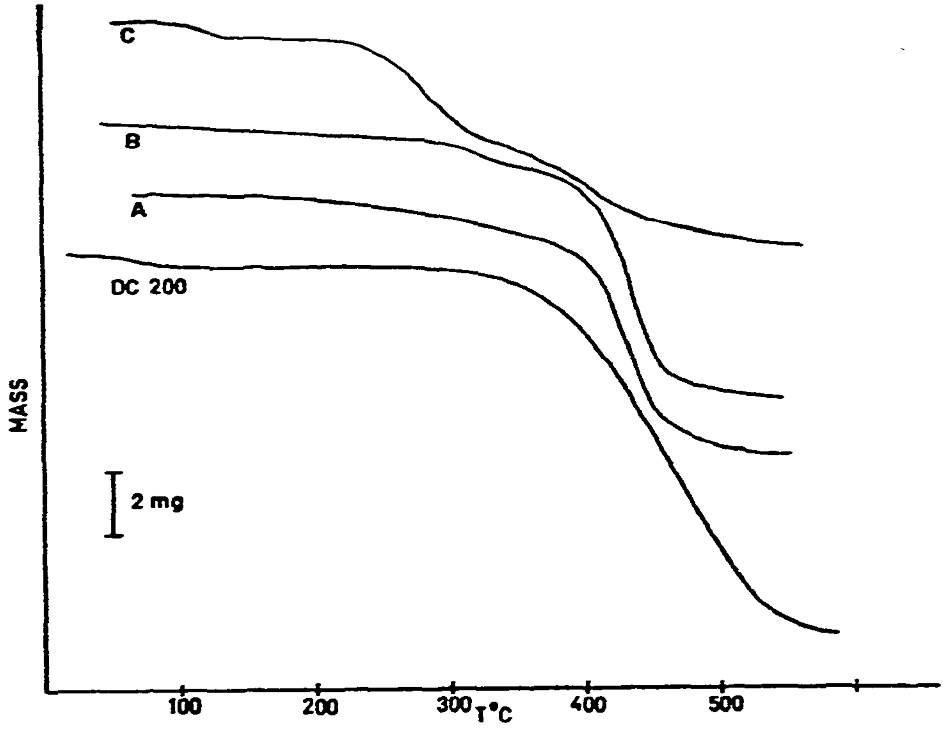


Fig. 2. TG curves of Silicone DC 200 and of chlorinated silicones samples A, B, C containing 15, 30 and 40% by weight chlorine, respectively.

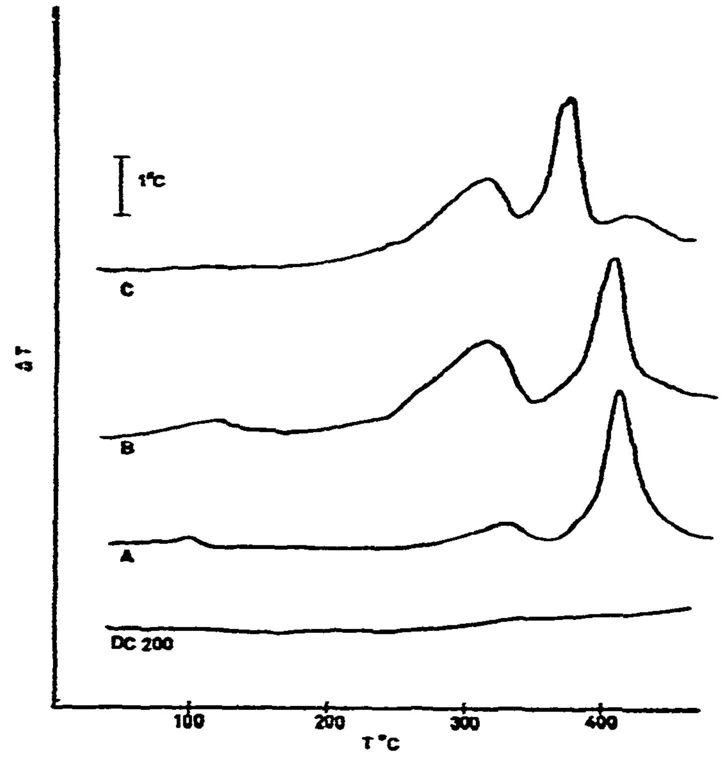


Fig. 3. DSC curves of Silicone DC 200 and of chlorinated silicone oil samples A, B, and C containing 15, 30 and 40% Cl by weight, respectively.

DSC and TG data were obtained on a Du Pont DSC Module and a Model 950 Thermobalance used in conjunction with the Model 990 Console. Sample weights ranged from 3 to 5 mg for DSC and from 8 to 12 mg for TG. A heating rate of 20°C min^{-1} was used. A nitrogen flow of 0.1 l min^{-1} was used for all samples.

RESULTS

Figure 1 shows the IR spectra of a silicone DC 200 fluid and of a chlorinated silicone containing 15% by wt. Cl (sample A). Figures 2 and 3 show TG and DSC traces of the silicone oil and of the three chlorinated samples. NMR data for the three samples are as follows:

Sample A: Multiplet (0.3 δ), singlet (2.7 δ); signal intensity 6.8:1.0.

Sample B: broad singlet (0.5 δ), broad doublet (3.0 δ), broad doublet (5.5 δ); signal intensity 16.7:6.2:1.0.

Sample C: broad singlet (0.6 δ), singlet (3.6 δ), triplet (6.0); signal intensity: 4.8:1.0:2.3.

DISCUSSION

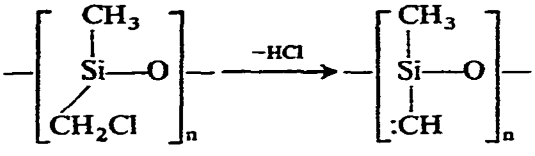
The IR spectrum of the silicone DC 200 is identical to the one reported by Hummel and Sholl[6]. The chlorinated DC 200 sample shows several new bands that can be assigned to C–Cl bonds in the 400–800 cm^{-1} region. NMR spectra reveal that at low chlorine contents (sample A) only two types of protons are present ($-CH_3$ and $-CH_2Cl$). As the amount of chlorine in the samples increases another signal possibly due to $-CHCl_2$ appears. This is in agreement with the observation that a Cl atom substitutes a H atom of a $-CH_2-Cl$ group more readily than that of a $-CH_3$ group[7]. Apparently, all three methyl protons can be substituted

TG curves indicate that the three chlorinated samples are less stable than the parent DC 200 fluid. However, these products tend to form more residue as the amount of chlorine in the samples increases. Sample C begins to lose weight around 120 °C, while the other samples lose very little weight up to 350 °C.

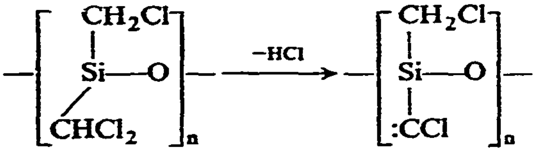
DSC curves show large exotherms for the three chlorinated samples, while for the DC 200 fluid only a slight change of baseline is noted. The DSC curves show that sample C is the least stable. A change of baseline is observed at 150 °C for this compound.

The three chlorinated samples turn yellow and liberate HCl at room temperature, TG, however, shows that the least stable compound starts decomposing appreciably around 120 °C.

Presently, there is insufficient information to suggest what might be occurring. Although for silicone oils it is commonly accepted that at high temperatures a depolymerization reaction occurs, the same may be only partially true for the chlorinated samples. The presence of three exotherms suggest that several things are occurring. The degraded samples resemble soot, and IR spectra of the residue reveal the presence of carbon–hydrogen bonds. It has been suggested[8] that the HCl liberated by these compounds cleaves the Si–O bond that is somewhat weakened by the presence of $-CH_2Cl$ and $-CHCl_2$ groups. If initially these compounds dehydrohalogenate, then the resulting species would be extremely unstable and in turn would lead to many different products.



or



Thus while in this report no definite conclusions can be reached on the degradation of chlorinated silicone oils, it does show that these samples decompose exothermally. This might suggest that a highly chlorinated silicone oil could have been an intermediate in one of the explosions that has been reported. Thus, if silicone oil leaked into a chlorine stream, the oil could be chlorinated to the point where it could decompose violently. The effect of metals on the decomposition of these compounds was not evaluated, and the synthesis of compounds with higher chlorine contents was not attempted.

CONCLUSION

The thermal stability of three chlorinated silicone fluids has been evaluated in a nitrogen atmosphere. The chlorinated samples decompose exothermally in a complex manner. This study shows TG and DSC data can be used to supplement data obtained from bomb calorimetry to evaluate potentially hazardous compounds.

ACKNOWLEDGEMENT

The author is indebted to the Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT), Caracas, Venezuela, for research grant number S-1-0481.

REFERENCES

1 R. R. McGregor, Silicones and Their Uses, McGraw-Hill, New York, 1954, pp. 39–41.
2 W. A. States, *Chem. Eng. Prog.*, 69 (1973) 52.
3 V. Bažant, V. Chvaloský and J. Rathovský, *Organosilicon Compounds*, Vol. I, Academic Press, New York, 1965, p. 270.
4 D. H. Rotenberg, Plasticization and Plasticizer Processes, Advances in Chemistry Series No. 48, *Amer. Chem. Soc. Publication*, 1965, p. 108.
5 F. J. Welcher (Ed.), Standard Methods of Chemical Analysis, Vol. II, Van Nostrand, New York, 1963, part 1, p. 389.
6 D. Hummel and F. K. Sholl, Infrared Analysis of Polymers, Resins and Additives: an Atlas, Vol. I, Wiley, New York, 1971, part 2, p. 1398.
7 R. H. Krieble and J. R. Elliot, *J. Am. Chem. Soc.*, 67 (1945) 1810.
8 E. E. Bostick, in E. M. Fettes (Ed.), Chemical Reactions of Polymers, *Interscience*, New York, 1964, p. 522.