SHORT COMMUNICATIONS

Three Crystalline Phases of Octachloropropane as Evidenced by Chlorine NQR

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(Received July 3, 1972)

In this communication, we wish to report the existence of three crystalline phases of octachloropropane (OCP), found by means of the NQR technique.

The experimental procedures of NQR measurements have been reported previously.[1] For the NQR experiments, a purified sample was used.[2] The sample was fused and packed in an ampoule.

The experimental results are given in Table 1, in which we can see that OCP posesses three crystalline phases (α, β, and γ). The phases were prepared by the following procedures:

The α phase. OCP was once sufficiently cooled at 77°K in the ampoule; next, it was left to stand at about 245°K and finally at 196°K for twenty minutes each. The last two procedures were repeated several times. Subsequent cooling in liquid nitrogen yielded the α spectrum.

The β phase. After the sample tube has been left to stand at room temperature for two days, it was immersed in a dry ice-petroleum ether bath (196°K) and then left to stand at the same temperature for two hours. Subsequent cooling in liquid nitrogen yielded the β spectrum.

The γ phase. After the sample has been once completely fused, the sample tube was immediately thrown into a dry ice-petroleum ether bath and left to stand at the same temperature for fifteen minutes. Subsequent cooling in liquid nitrogen yielded the γ spectrum.

The NQR spectrum of OCP has already been reported by Zeil and Haas.[3] Their results are also shown in Table 1. It can be seen in Table 1 that none of the three spectra, α, β, or γ, coincide with the Zeil's results. After certain annealings, we frequently observed an NQR spectrum corresponding to a mixture of the α and γ phases.[4] In this connection, it should be noted that Zeil's results are in rather good agreement with a superposition of the lower-frequency parts of the α and γ spectra.

Our DSC experiments showed that OCP posesses a plastic crystalline phase at room temperature (mp: *ca.* 433°K, ΔH_{mp}: *ca.* 560 cal/mol, and ΔS_{mp}: *ca.* 1.3 e. u.).[5] This is consistent with the apparent plasticity of OCP at room temperature and with the fact that the NQR signals were not observed at room temperature.[6,7]

Details of the NQR and DSC studies will be reported in a later publication.

TABLE 1. ^{35}Cl NQR FREQUENCIES OF OCTACHLOROPROPANE AT LIQUID NITROGEN TEMPERATURE

	No.	Frequency (MHz)	Relative Intensity
α Spectrum[a]	ν_1	41.457	4
	ν_2	41.322	4
	ν_3	41.261	4
	ν_4	41.183	10
	ν_5	41.089	2
	ν_6	40.991[b]	6
	ν_7	40.991[b]	6
	ν_8	40.764	4
β Spectrum	ν_1	41.454	10
	ν_2	41.270	3
	ν_3	41.173	8
	ν_4	41.112	8
	ν_5	40.994	4
	ν_6	40.890	6
	ν_7	40.845	10
	ν_8	40.795	6
γ Spectrum	ν_1	41.570	10
	ν_2	41.445	8
	ν_3	41.069	7
	ν_4	41.060	7
	ν_5	40.932	6
	ν_6	40.857	6
	ν_7	40.760	6
	ν_8	40.643	6
Zeil's result[c]		41.180	
		41.056	
		41.046	
		40.932	
		40.850	
		40.765	
		40.750	
		40.637	

a) The intensity of the α spectrum is so much stronger than those of the β and γ spectra that all the resonance lines were observable on an oscilloscope screen. b) This degeneracy was confirmed by the temperature dependence of the resonance frequencies. c) Ref. 3.

1) M. Hashimoto and K. Mano, This Bulletin, **45**, 706 (1972).

2) The gas chromatographic analysis of the sample showed a purity of approx. 99.5%.

3) W. Zeil and B. Haas, *Z. Naturforsch.*, **23a**, 1225 (1968).

4) After certain annealings the DSC curves on heating (from 113 to 253°K) showed four thermal anomalies, one of which was observed as an exothermic peak. The results of the DSC experiments, however, are rather complicated and depend strongly on the thermal conditions. This may be correlated to the observations of the superpositions of the NQR spectra.

5) J. Timmermans, *J. Chim. Phys.*, **35**, 331 (1938).

6) H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **32**, 548 (1960).

7) S. Kondo, This Bulletin, **39**, 249 (1966).