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STUDIES ON THE CHARACTERISTICS OF THE ISOMERS OF HEXACHLOROCYCLOHEXANE (HCCH) BY THERMOGRAVIMETRY

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A new method of determination of HCCH isomers by thermogravimetry is described. The thermal changes of the isomers, the decomposition characteristics and the parameters for identification are discussed.

Hexachlorocyclohexane (HCCH) is an extensively used organochlorine compound in pest-control measures. HCCH consists of several isomers, including the recently-isolated isomer X_3 [1]. Among the isomers, the *gamma* isomer, also known as Lindane, is an insecticidal component of HCCH, whereas the other isomers have low or no insecticidal value, but high mammalian toxicity. The known methods of identification of these isomers are determination of the melting point, and thin-layer and gas-chromatography. TG and DTG studies were carried out on some of these isomers to determine their pattern of decomposition and to correlate with other properties in relation to their specificity.

Experimental

Standard alpha (α), beta (β) and delta (δ) isomer samples obtained from E. Merck AG Darmstadt and the gamma (γ) isomer from Fluka Chemische AG. were used in the present study. Isomer X_3 was isolated from technical BHC (benzenehexachloride) in this laboratory.

TG was carried out on pure isomers, using a TG apparatus described elsewhere [2]. It was calibrated with AR calcium oxalate.

250 mg of the isomer was taken in a 10 cc conical porcelain sample holder, covered with a mica cap having a 2 mm dia orifice as an outlet to obviate pressure build-up of the evolved gases. The samples were heated in a static air atmosphere in a vertical furnace at a rate of $5 \pm 0.3°$/min, using an Electroflo cam-type programmer. A quartz LCD stopwatch was used as a check for linear heating. The weight changes were recorded by a Sartorius thermobalance up to a temperature of 350°. The results were confirmed by replication.

Results and discussion

The TG and DTG curves of the samples investigated revealed a distinct decomposition pattern for each isomer (Figs 1 and 2). The thermal properties of the isomers, along with the melting points [3] and R_f values obtained by TLC (M. Jayaram – personal communication), are presented in Table 1. It is seen from the results that the initial temperatures (T_i), while being same for the δ and X_3 isomers, were very close for γ and α, whereas the β isomer showed a T_i of 160°. The final temperature (T_f) for all the isomers tested ranged from 280–312°, with the β isomer showing the highest value. The reaction interval observed was longest for β and shortest for δ. The temperatures at which the half-weight losses of the samples occur were distinctly discernible.

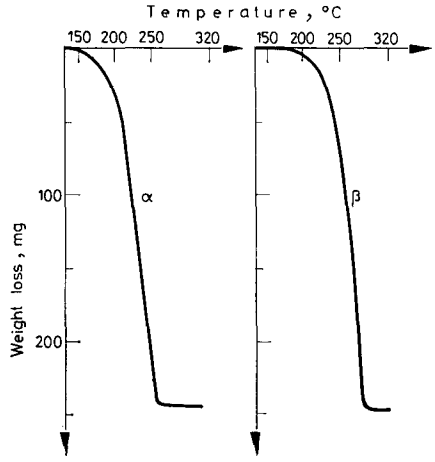

Fig. 1. TG curves of α and β isomers

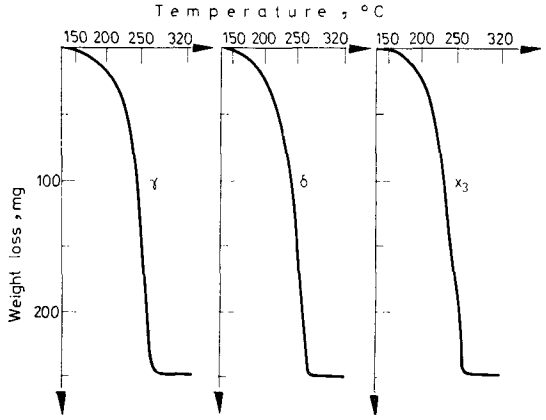

Fig. 2. TG curves of γ, δ and X_3 isomers

DTG curves (Figs 3 and 4) revealed a unique decomposition pattern for each isomer. Major and minor decomposition steps were noticed for all isomers. Six decomposition steps were observed for β, five steps for γ, four steps for δ and α, and three steps for X_3. Major thermal decomposition of the isomers occurred between 190 and 280°. Many smaller inflections were noticed during minor decomposition. The peak height and temperature of each decomposition step were very characteristic and could be used for the identification of the isomers. Significant differences between the insecticidal γ isomer and the undesirable β are the major decomposition steps at 244 and 264° for γ, and at 262 and 288° for β. Other isomers also exhibited distinct decomposition reaction steps and peak height differences (Table 1).

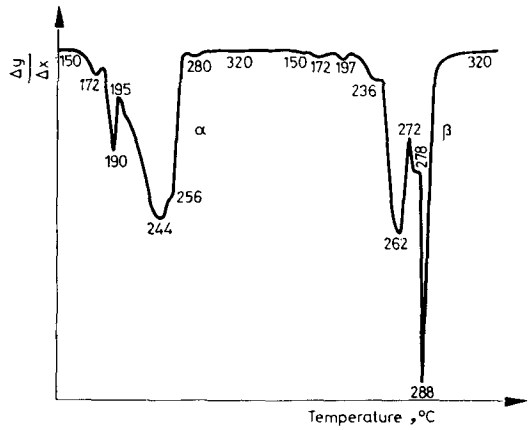

Fig. 3. DTG curves of α and β isomers

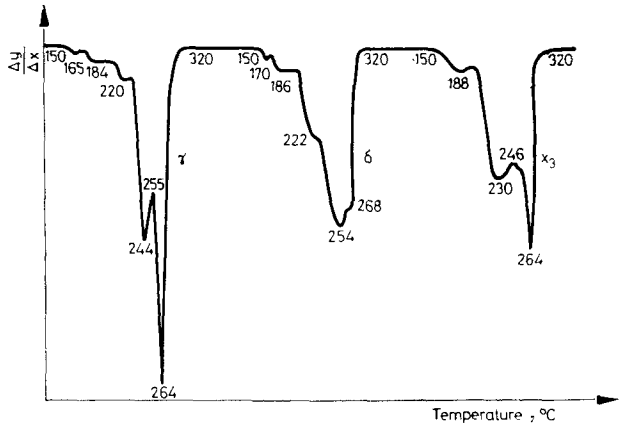

Fig. 4. DTG curves of γ, δ and X_3 isomers

Table 1

Thermal and other properties of HCCH Isomers

Isomer	Melting point, °C	T_i, °C	T_f, °C	Half-weight loss temp., °C	R_f value*	Reaction interval, °C	Decomposition steps °C/Peak height, mm	
Alpha	158.5	154	288	229.0	0.33	134	190/35	172/6
							244/84	280/3
Beta	309	160	312	258.5	0.19	152	262/65	172/3
							288/142	197/4
								236/5
								278/8
Gamma	112.8	156	290	246.0	0.26	134	244/60	165/5
							264/142	184/7
								220/7
Delta	139	162	280	239	0.09	118	222/15	170/4
							254/21	186/7
X_3	76	162	284	233.5	0.45	122	230/32	188/9
							263/80	

* Solvent system: Cyclohexane.

There have previously been no reports on the thermal decomposition of HCCH isomers. Isomer identification was performed earlier by melting point determination, and more recently by TLC and GC. While the melting point is fairly different for each isomer, R_f values are very close to each other. However, Wendlandt and Zief [4] and Duval [5] have doubted the consideration of melting point as a fundamental value, since many organic compounds lose weight below their melting point.

In the present study all the isomers except β and α lose weight well above their melting point, suggesting that γ, δ and X_3 decompose in the liquid phase, while β and α decompose in the solid phase. As the decomposition proceeds, α and β enter the liquid phase at 159° and 309°, respectively. This suggests a solid-liquid phase type decomposition for these two isomers. However, β seems to be in the solid phase over a longer period during the thermal decomposition, whereas α has a prolonged liquid phase decomposition. Although the exact mechanism of decomposition is not known, a series of complex reactions seem to take place at a rapid rate in different thermal steps of decomposition, followed by the evolution of gases; this results in the disintegration of the organic molecule at T_f, and finally the compound is reduced to carbon [6] around 310°, which persists till 350°. Above this temperature, no material is left in the sample holder.

Thus, this study has demonstrated for the first time the use of thermogravimetry (TG) and derivative thermogravimetry (DTG) for the identification of HCCH isomers. The important parameters for the identification of the isomers

are the decomposition steps and peak heights, the reaction interval, the half-weight loss temperature and T_f. The study also opens up the possibility of using TG and DTG for the identification of other chlorinated pesticides.

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RÉSUMÉ — On décrit une nouvelle méthode de détermination des isomères HCCH par thermogravimétrie. On discute les modifications thermiques des isomères, les caractéristiques de décomposition et les paramètres d'identification.

ZUSAMMENFASSUNG — Eine neue Methode der Bestimmung von HCCH-Isomeren durch Thermogravimetrie wird beschrieben. Die thermischen Änderungen der Isomere, die Zersetzungscharakteristika und die Identifizierungsparameter werden erörtert.

Резюме — Описан новый метод определения изомеров гексахлороциклогексана с помощью термогравиметрии. Обсуждены термические изменения изомеров, характеристики их разложения и параметры их идентификации.