

Comparative study of thermal and CO₂-laser-induced pyrolysis of 1,2-dichloropropane in excess of boron trichloride

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The effect of an excess of boron trichloride upon the products distribution in thermal and CO₂-laser-induced pyrolysis of 1,2-dichloropropane was examined. Only small variations in the yield of some products were found, which presumes no strong specific BCl₃...1,2-dichloropropane interaction during the pyrolyses.

Исследовано влияние избытка треххлористого бора на соотношения продуктов термического и индуцированного CO₂-лазером пиролиза 1,2-дихлорпропана. Были найдены лишь незначительные отличия в выходах некоторых продуктов, что свидетельствует об отсутствии сильного специфического взаимодействия BCl₃...1,2-дихлорпропан во время пиролиза.

Industrial propylene oxide production suffers from the side reaction leading to 1,2-dichloropropane [1]. The latter compound is practically considered a waste product and any type of its selective conversion is desirable. The study of thermal and laser pyrolysis of 1,2-dichloropropane presented in this paper was stimulated by an effort to look whether the 1,2-dichloropropane decomposition can be catalytically affected by the excess of boron trichloride.

Thermal decomposition of 1,2-dichloropropane has been studied in detail as a process occurring in conventional (surface, 500—860 K) reactors [2—4] and as a reaction induced in a shock-tube or initiated with infrared laser (experiments free from surface effects, 900—1100 K) [5]. In surface-less reactions, 1,2-dichloropropane decomposes mainly by a four-centre (molecular) elimination of hydrogen chloride affording four primary reaction products, 3-chloropropene, 2-chloropropene, and *cis*- and *trans*-1-chloropropenes, together with minor quantities of methane and C₂ compounds. In surface reactors the formation of the four isomeric chloropropenes is accompanied with that of propene; propene and 3-chloropropene undergo complex (probably radical-chain) consecutive reactions the extent of which increases [3] with higher temperature and conversion.

As for the chloropropenes, their distribution is similar in both surface ($T > 670$ K) and surface-free (laser sensitized or unsensitized) processes, 3-chloropropene being favoured over 1-chloropropenes, and 2-chloropropene being formed in the lowest yield. The formation of 2-chloropropene can be, similarly as that of propene, somewhat increased in surface, unseasoned packed (Pyrex) reactor.

Considering the earlier reported data [2—5] on 1,2-dichloropropane decomposition, the process does not appear to be easily made to significantly favour one of a few products.

In the present report an attempt has been made to affect the products distribution by conducting the 1,2-dichloropropane thermal decomposition in the presence of boron trichloride. This compound acting as a strong Lewis acid, used as a sensitizer in CO_2 -laser-induced chemistry and having a special effect upon the course of some CO_2 -laser-photosensitized (BCl_3) reactions [6, 7] might affect the nature of the transition state of the decomposition due to its acidic properties or its vibrational excitation. The decomposition of 1,2-dichloropropane in the presence of BCl_3 was carried out as thermal or CO_2 -laser-induced process.

Experimental

For laser-powered decomposition a cw CO_2 laser [8] operated at the P(24) line of the $00^0_1 \rightarrow 10^0_0$ transition (940.55 cm^{-1}) was used to vibrationally excite boron trichloride. The laser beam was focused with a 10 cm focal length Ge lens 4 cm after the entrance NaCl window of the stainless steel tube-like reactor (11 cm long, 2.4 cm I.D.) equipped with two NaCl windows and a valve. In a typical run the reactor was filled with a mixture of 1,2-dichloropropane and boron trichloride pre-prepared on a standard vacuum line, the sample was irradiated, and the extent of the decomposition was followed by gas chromatography.

The conventional (static) pyrolysis of 1,2-dichloropropane or its mixtures with boron trichloride was carried out in an electrically heated Simax ampoule (90 cm^3 in volume) closed with a P.T.F.E. stopcock. First runs (No. 1, 2) concern the decomposition with an unseasoned surface, experiments No. 3—7 relate to the surface coated with carbon (aged surface).

Gas chromatography analysis of the decomposition progress was made with Chrom-5 instrument (FID detector, carrier gas nitrogen, and programmed temperature — 6 min 45°C , $3^\circ\text{C}/\text{min}$ up to 100°C) making use of the reported [9] irreversible absorption of BCl_3 on silicon elastomer. The column was filled with 15 % FS-16 silicon elastomer (0.6 m) and 20 % dinonyl phthalate (3.7 m) on Chromaton N-AW (0.20—0.25 mm). The mixtures from the reactors were transferred by means of the vacuum line into ampoules which were furnished with P.T.F.E. stopcock and a side arm with rubber septum by freezing the ampoules with liquid nitrogen. After the equalling the pressure in the

Table 1

Conventional pyrolysis of 1,2-dichloropropane (4 kPa) at 733 K

Run	Time min	Relative peak area/%							Isomer ratio ^a		
		A	B	C	D	E	F	G	<i>n</i> (3-CP): <i>n</i> (2-CP)	<i>n</i> (3-CP): <i>n</i> (1-CP)	<i>n</i> (<i>cis</i> -1-CP): <i>n</i> (<i>trans</i> -1-CP)
1	6	1.4	1.3	1.4	0.6	2.4	0.5	92.4	1.9	1.2	2.3
2	22	5.1	4.5	22.6	10.0	49.2	—	8.0	10.9	1.5	2.3
3	15	9.8	0.6	7.3	3.6	14.2	0.4	64.0	23.6	1.3	2.0
4	30	30.8	2.2	17.6	9.2	19.3	7.4	12.4	8.8	0.7	1.9

a) CP = chloropropene.

Table 2

Conventional pyrolysis of 1,2-dichloropropene (4 kPa) in mixture with BCl₃ (12 kPa) at 733 K

Run	Time min	Relative peak area/%							Isomer ratio ^a		
		A	B	C	D	E	F	G	<i>n</i> (3-CP): <i>n</i> (2-CP)	<i>n</i> (3-CP): <i>n</i> (1-CP)	<i>n</i> (<i>cis</i> -1-CP): <i>n</i> (<i>trans</i> -1-CP)
5	5.5	4.1	0.2	1.7	0.7	3.4	0.5	89.1	17	1.4	2.4
6	9	3.3	1.1	9.7	3.9	18.2	0.4	62.8	16.5	1.3	2.5
7	30	1.8	2.7	19.1	9.7	41.7	2.8	21.8	15.4	1.4	2.0

a) CP = chloropropene.

Table 3

CO₂-Laser-photosensitized (BCl₃) pyrolysis of 1,2-dichloropropane^a

Run	Time of irradiation s	Focused	Relative peak area/%							Isomer ratio ^b		
			A	B	C	D	E	F	G	<i>n</i> (3-CP): <i>n</i> (2-CP)	<i>n</i> (3-CP): <i>n</i> (1-CP)	<i>n</i> (<i>cis</i> -1-CP): <i>n</i> (<i>trans</i> -1-CP)
8	20	yes	—	0.5	6.0	3.4	15.5	—	71.9	31.0	1.6	1.8
9	40	yes	0.4	1.1	13.5	8.0	32.2	—	43.8	29.2	1.5	1.7
10	60	yes	0.9	1.3	18.9	10.6	43.1	—	24.9	33.2	1.5	1.8
11	120	yes	1.8	1.7	23.0	13.0	51.3	—	8.2	30.2	1.4	1.8
12	20	yes	2.1	0.5	6.7	3.0	13.9	—	71.2	27.8	1.4	2.2
13	50	yes	7.0	1.7	23.0	11.9	41.1	—	9.2	24.2	1.2	1.9
14	150	no	0.5	1.3	18.8	9.9	40.2	0.9	29.1	31.0	1.4	1.9

a) Runs 8—11: 3.5 W laser output, 12 kPa BCl₃, 4 kPa C₃H₆Cl₂; Runs 12, 13: 3 W laser output, 28 KPa BCl₃, 1.3 kPa C₃H₆Cl₂; Run 14: 5 W laser output, 12 kPa BCl₃, 4 kPa C₃H₆Cl₂.

b) CP = chloropropene.

ampoules with gaseous nitrogen to atmospheric pressure, the samples for GC analysis (0.5 cm^3) were taken through the septum *via* syringe.

The assignment of GC peaks in pyrolysis mixtures to chloropropene isomers was made on the basis of their known ratio under reported [4] conditions (4 kPa, 460°C). The GC peaks with 3-chloropropene, propene, and benzene were identified by comparing retention times with standard samples (chloropropene and propene (Fluka, A.G.), benzene (Lachema, Brno)). The same technique with propyne and allene (both Matheson) showed these compounds to give GC peak closely behind that of propene.

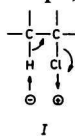
All results gathered in Tables 1—3 represent average of two measurements at least.

Results and discussion

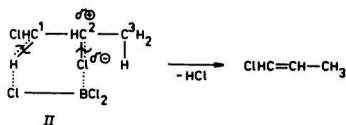
The Arrhenius parameters of three of the four reactive channels of 1,2-dichloropropene decomposition, that is the formation of *cis*- and *trans*-1-chloropropene and 3-chloropropene, are very close to each other [2—5]. The temperature variation cannot therefore be an effective way to dramatically increase the yield of one of chloropropenes at expenses of others. It may, however, be that only one channel of the decomposition can be made important *via* a strong interaction of 1,2-dichloropropene with a catalyst. Boron trichloride is one of a few possible suitable compounds.

The scrutiny [10] over the literature shows that BCl_3 is vastly used as a catalyst of organic reactions or as a reagent in reactions with organic compounds. Having in account its possible reactions with 1,2-dichloropropene or with products of its thermal decomposition, paying the attention to BCl_3 reactions with alkyl chlorides or olefins is appropriate. BCl_3 can add to unsaturated compounds with electronwithdrawing substituents [11] (which are chloropropenes as well), induce polymerization of olefins [12], be a catalyst for cyclo-trimerization of tetrachloroethylene [7], and exchange halogens with tetrafluoroethylene [13]. As for the BCl_3 reactions with alkyl chlorides, despite that interactions between electrophilic catalysts and alkyl halides are commonly assumed to occur in solution [14], there is, surprisingly, only one report on BCl_3 reaction with alkyl chlorides, namely [15] tropylium salt formation from *tert*-butyl chloride and cycloheptatriene enhanced with BCl_3 ability to bond further chlorine.

Thermal decomposition of alkyl halides is also enhanced by interaction of alkyl halide with polar or metal surfaces [16] or with vaporized alkali metals [17]. While the last effect involves radical steps, the effect of polar and metal surfaces



can be visualized *via* structure *I* wherein, depending upon the catalyst (surface), rupture of either C—H or C—halogen bond can be promoted. Should similar interaction R—Cl... BCl₃ occur in the gaseous phase with 1,2-dichloropropane, it can be regarded as (1) BCl₃ assisted C—Cl bond dissociation ensued by C—H bond cleavage (nonconcerted process), or as (2) synchronous C—Cl and C—H bonds cleavages taking place in 6-membered structure like *II*, wherein the C³—H cleavage should be favoured over that of the C³—H bond.



The first mechanism cannot result in a different product distribution, the second one should, on the electronic grounds, favour the formation of 1-chloropropenes.

The third effect of BCl₃ can also be possible. It was observed in some [6, 7] reactions induced with CO₂ laser, and despite that it was not interpreted in sufficient detail, it is believed to consist in a vibrationally enhanced catalytic nature of BCl₃. These assumptions spurred the study of 1,2-dichloropropane thermal decomposition in excess of BCl₃ presented below.

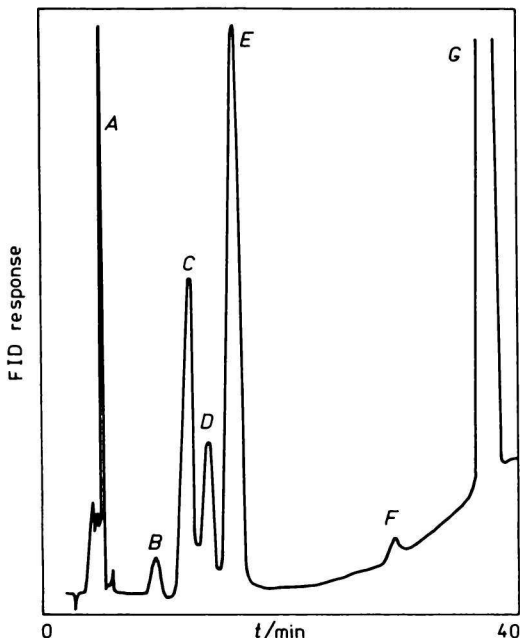


Fig. 1. Chromatogram of conventional pyrolysis of 1,2-dichloropropane (Run 3, Table 1).

In an effort to reference the peaks in the GC chromatogram of the products mixtures after the pyrolysis of 1,2-dichloropropane in the presence of BCl_3 , the conventional decomposition of 1,2-dichloropropane under conditions with which chloropropene isomers are produced in known ratios [3] was carried out first (Table 1). Typical GC record is given in Fig. 1 and the peaks designated therein as A—G were assigned as:

A — propene; B — 2-chloropropene; C — *cis*-1-chloropropene; D — *trans*-1-chloropropene; E — 3-chloropropene; F — benzene; G — 1,2-dichloropropane.

Thereafter, the decomposition of 1,2-dichloropropane in excess of boron trichloride induced thermally in an aged Simax vessel at the same temperature as the decomposition without BCl_3 was examined. The results are given in Table 2 and show that the distribution of chloropropene isomers resembles that in the decomposition without BCl_3 . The same is also true with the decomposition in an excess of BCl_3 conducted as a laser-induced process (Table 3), where the only slight difference in the chloropropene isomers ratio is a slight decrease of 2-chloropropene yield.

Along with chloropropenes, benzene, propene and, apparently, also propyne together with allene appear to be formed. Last three compounds can be considered the products of 3-chloropropene decomposition [18]. As for these compounds, the yield of propene and of the products of 3-chloropropene consecutive decomposition is decreased in an excess of BCl_3 . These results, though only of qualitative nature, show that (1) the effect of BCl_3 on the distribution of products in thermal decomposition of 1,2-dichloropropane is small and that (2) no aforementioned specific strong interaction between BCl_3 and 1,2-dichloropropane and/or chloropropene exists.

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