Decomposition of Trichlorobenzene Isomers by Co-Grinding with CaO

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Two types of trichlorobenzene (TCB) isomers, 1,2,3- and 1,3,5-, were subjected to grinding in air with CaO in a planetary ball mill to investigate their decomposition phenomena. Results showed that TCB samples were decomposed by the co-grinding to form calcium chloride hydrate and amorphous carbon as the main products, with other minor compositions such as carbon dioxide and water. There was no significant difference in the decomposition phenomena between the two isomers. Radicals were generated during the decomposition process, predominantly due to the rupture of C–Cl bonds in the molecule. Supported by the simulation data, we concluded that dehydrochlorination during TCB decomposition process to form hydrochloride (HCl, further to CaOHCl) exhibited the lower possibility, suggesting dechlorination rather than dehydrochlorination as the plausible decomposition pathway.

The incineration of chlorinated organic compounds or halogen-containing substances has some potential to form hazardous compounds such as harmful gases and dioxins. This has initiated interest in the development of decomposition technologies for such chlorinated materials and wastes. Several methods have been proposed, but inherent problems with safety, reliability, operational costs and the like persist. Recently, Zhang et al. have proposed a method for decomposing such halogenated organic compounds: namely, a mechanochemical method based on grinding with an inorganic material such as CaO. The decomposition is induced through the solid-state reaction between the organic and inorganic compounds,[1–5] and when the chlorinated organic compound is, for example, ground with CaO, the chlorines are transformed into inorganic chloride. All the same, the mechanochemical method is a nonthermal process, similar to those for the photo-induced and radiation-induced catalytic methods.[6,7] However, a decomposition mechanism based on a mechanochemical method remains to be determined. It is easy to imagine that such a decomposition of chlorinated organics on the surfaces of inorganic additives would be very complex so that it would be difficult to interpret the phenomena observed and the reaction mechanism by one simple pathway. In order to simplify the problem, discussion on the reaction mechanism was focused on whether it proceeded through a dechlorination or a dehydrochlorination, since such a controversy was met before during our work on the decomposition of chlorobiphenyl, a model sample of PCB and dioxin, and needs further investigation. Here, trichlorobenzenes ($C_6H_3Cl_3$, TCB) were chosen as the target sample for several reasons. A solid state of TCB did not limit the amount used, which occurred in the case of PCB of liquid state, because a dry grinding is preferred. Another important reason came from the result that a greater amount of HCl, namely CaOHCl as product, can be obtained than from any other chlorinated aromatic compounds, if the so-called dehydrochlorination occurred.

Such phenomena were elucidated further by a computational chemical process, which is a useful tool for understanding intermediate states and unstable conditions during chemical reactions. In addition, this process is advantageous for handling hazardous and toxic substances as well as directly analyzing the phenomena which are happening.[8–12] There have been two typical methods proposed, namely a classical mechanics method and a quantum mechanics method. And the quantum mechanics method is classified into a non-experimental method and a semi-empirical molecular method. The former is a kind of non-empirical method called an ab initio method, that enables us to reveal reaction mechanisms which are related to various electronic and excitation states between two components such as metallic and organic ones without any experimental parameters.[13] However, the method is not always suitable for a compound with large molecular weight because it requires a lengthy time for calculation. In contrast, the latter method, called a semi-empirical molecular method, is suitable for compounds with large molecular weight like organic molecules, while it can also be successfully used for inorganic compounds.[14–16]

The purpose of this paper is to provide information on a TCB decomposition reaction based on both experimental results and computational chemical simulations. As a result, the decomposition of TCB is interpreted through a pathway of dechlorination rather than dehydrochlorination. It is expected that a combination of computational chemical simulation and practical experimental method will prove useful for this kind of study.

Experimental

Experimental Procedure and Characterizations. 1,3,5-TCB sample (Tokyo Kasei Kogyo, Ltd., Japan) and 1,2,3-TCB sample (Wako Pure Chemicals Ltd., Japan) were used. The TCB samples were mixed with the CaO powder at a 1:12 molar ratio. The CaO sample was prepared by heating calcium hydroxide (Ca(OH)$_2$ (Wako Pure Chemical Industries, Ltd. Japan)) at 800 °C for 2 h in air in an electric furnace. The mixture of 2 g (0.43 g TCB + 1.57 g CaO) was ground by a planetary ball mill (Fritsch Pulverisette-7, Germany) in air at 700 rpm for various periods of time. The mill is composed of pair of pots made of zirconia; each pot has an inner volume of 45 cm^3. Seven zirconia balls of 15 mm diameter were charged in the pot together with the mixture, and then the mill was operated. To prevent excess heating, the milling was stopped for 15 min after every 15 min grinding operation.

The ground samples were characterized as follows: X-ray diffraction (XRD) (RAD-B system, Rigaku, Japan) using Cu-Kα radiation was used to identify phases formed in the ground product. Raman spectra (Labspec Raman spectrograph, Horiba) were recorded at room temperature with a helium laser beam at 632 nm line. Samples for ESR analysis were charged in a quartz tube of 5 mm diameter, and measurements were carried out with an X-band ESR spectrometer (Bruker ESP-380E).

The gas composition was analyzed by GC/MS. The gas was drawn by a syringe just after stopping the mill and inserted into the spectrometer for analysis using a Hewlett-Packard gas chromatograph (model 6890) equipped with a mass selective detector (model 5973). The ground samples were also washed with water, acetone, or toluene as follows: 0.5 g samples were agitated in 100 mL distilled water or 50 mL acetone or toluene with a magnetic stirrer for 30 min to extract chemicals into the solution. After filtration, the filtrates were subjected to ion chromatography (IC) (LC10series, Shimadzu Co. Ltd.) and GC/MS analysis (the same spectrometer).

Computational Chemical Work. The semi-empirical molecular orbital method was used during the computational chemical calculation. The calculation software was winMOPAC ver. 3.0 (FUJITSU). PM3 (Parametric Method-3) was adapted for the semi-empirical Hamiltonian.[17,18] Original structures of the molecules were calculated by geometry optimization methods. The same method was adapted for the calculation of bond energy, except for the aimed bond. The length of the bond was fixed for 0.02 nm longer than the original structure, and the difference from original internal energy was defined for each "bond energy". This difference also represents the strength of the bond. Furthermore, the reaction barrier was calculated by the same procedure. The length of the bond was stretched until it was 0.2 nm longer than the original structure, and the internal energy was calculated every 0.02 nm. The reaction barrier was defined as the maximum difference from the original internal energy. In this paper, the highest reaction energy until 0.2 nm was defined for each "barrier energy". If the difference energy did not converge until 0.2 nm, the reaction energy was equal to the energy of the structure whose bond length was 0.2 nm longer than the original structure, defined as the "final energy".

Results and Discussion

Experimental Part. Figure 1 shows the yield of the remaining TCBs in the ground samples as a function of the grinding time. As shown in the figure, the yields decrease rapidly with the grinding time in the early stage, and level off dur-
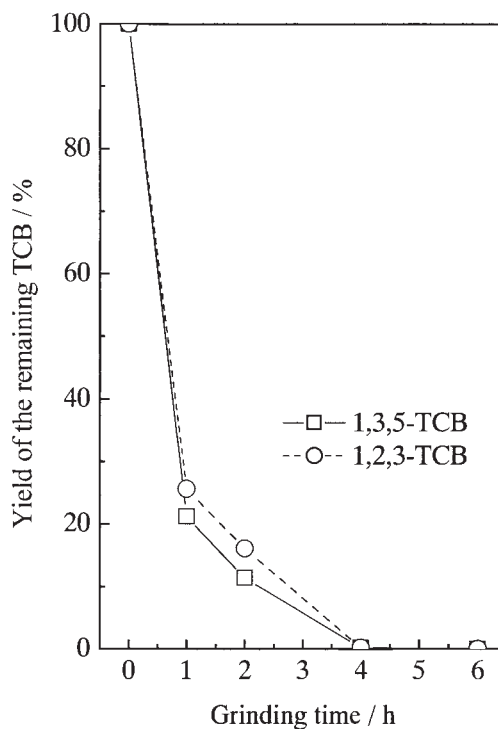

Fig. 1. Yield of TCB remaining in the ground mixture as a function of grinding time.
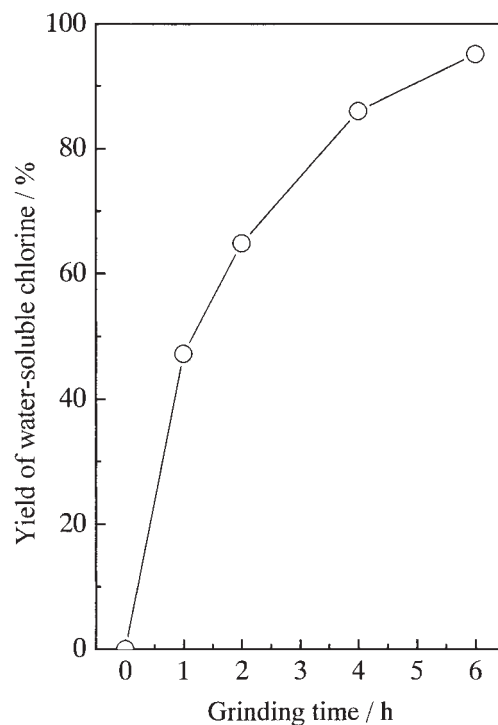

Fig. 2. Yield of water-soluble Cl in the ground mixture as a function of grinding time.

ing the prolonged grinding. Finally, the yield reaches 0% at 6 h grinding. This indicates that the TCB samples can be decomposed under this grinding condition within 6 h. Between the two TCBs, there exists little difference in decomposition yield and other experimental results, although this data is not

shown here. Therefore, the following results resulting from the 1,3,5-TCB sample are presented.

Figure 2 shows the yield of water-soluble chloride formed in the ground product as a function of grinding time. The yield is defined as (Cl_m/Cl_t), where Cl_m denotes the concentration of Cl ions in the filtrate measured and Cl_t is the concentration of Cl in the TCB sample. As has been indicated in the figure, the yield increases rapidly with an increase in grinding time and reaches about 95% within 6 h grinding. It is clear that the organic chlorine has been changed into an inorganic water-soluble compound, consistent with the results shown in Fig. 1.

Figure 3 shows GC/MS spectra of the substances extracted by toluene from the TCB ground samples. In the spectrum of the sample ground for 1 h, a strong peak corresponding to the original TCB sample has been observed, together with other very small peaks. When the grinding time is extended to 6 h, only little peaks due to benzaldehyde (C_6H_5CHO) and 1,3,5-TCB are detected from the spectrum. Zero percent to the original TCB was obtained by the calculation based on the peak area, indicating that the decomposition of TCB sample has been almost completely achieved by this time. The results obtained by using acetone as solvent are almost the same as the above results.

From the spectrum of 1 h ground sample, several small peaks are observed, suggesting the existence of some intermediate phases from the TCB decomposition. Since the effect of tiny impurities from the solvent itself can not be ruled out completely, it is more reasonable to directly analyze the compositions of gases in mill pot to get the information about the intermediate phases. Figure 4 shows the GC/MS spectra of the gases collected from the pot just after grinding. It is very interesting to note that many compounds such as TCB, tetrachlorobenzene (TeCB), dichlorobenzene (DCB), chlorobenzene (CB), toluene ($C_6H_5CH_3$) and benzene (C_6H_6), are observed from the gas at 1 h grinding. And these phases have disappeared when the grinding time is extended to 6 h, where only a little peak due to TCB is observed to remain. The analysis using different columns showed that gases with low molecular weight, such as H_2O, ethane (C_2H_6), ethylene
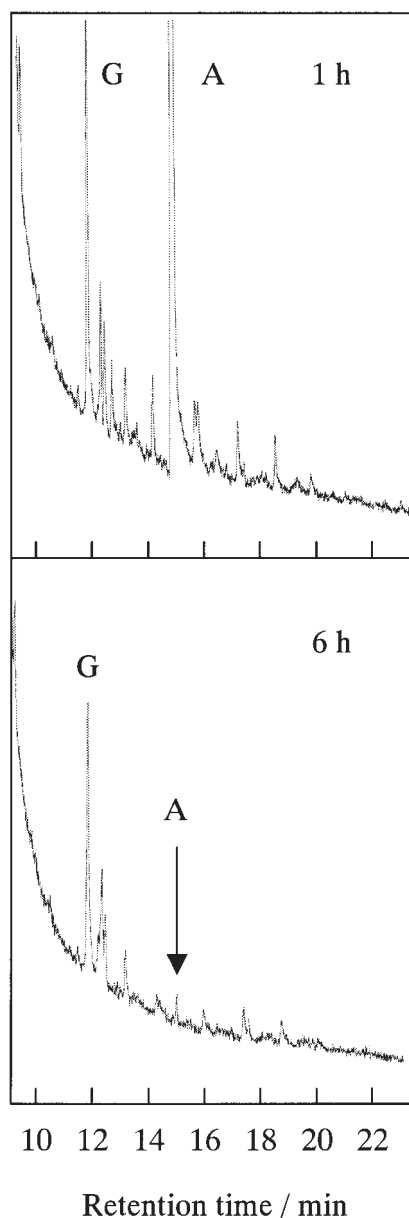
Fig. 3. GC/MS spectra of the substances extracted from ground products by toluene. A: Trichlorobenzene, G: Benzaldehyde.
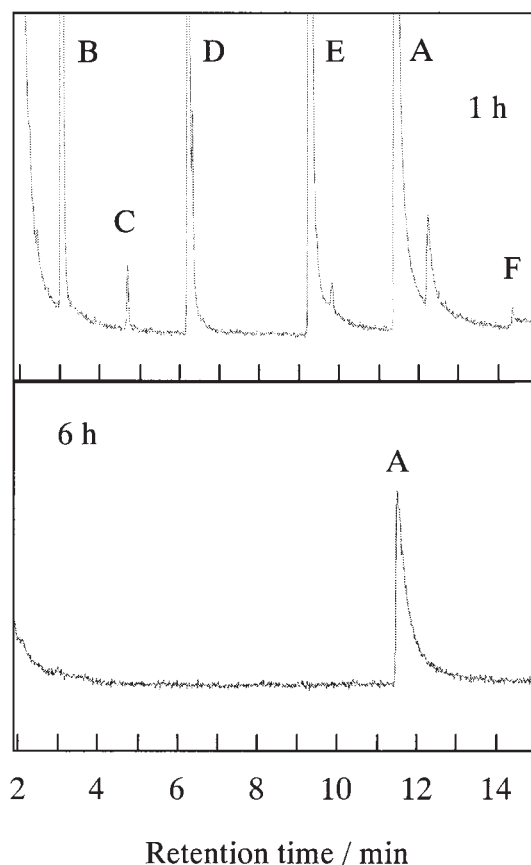
Fig. 4. GC/MS spectra of gases collected from the mill pot after 1 h and 6 h grinding. A: Trichlorobenzene, B: Benzene, C: Toluene, D: Chlorobenzene, E: Dichlorobenzene, F: Tetrachlorobenzene.

(C_2H_4) (only 1 h ground sample), carbon dioxide (CO_2) and methane (CH_4), were formed irrespective of the grinding time. Since no gas pressure has been observed, these gases should be present in tiny amounts. Except the tiny amount of TCB, all other chlorine-containing intermediates have been found to disappear by the prolonged grinding up to 6 h. Both GC/MS data sets shown in Figs. 3 and 4 confirm the existence of so many intermediate phases, suggesting that the mechanochemical process of decomposition is very complex, possibly with various pathways. Fortunately, it separates chlorine from benzene ring at the beginning of decomposition and these intermediate compounds have disappeared from the sample by prolonged grinding, indicating that they are also decomposed together with the TCB during the further grinding operation.

Figure 5 shows the Raman spectra of the TCB ground samples. The Raman shifts at 1570 and 1310 cm^{-1} bands from amorphous carbon[19–21] are observed and the peak intensity gets higher with the increase in grinding time, indicating the occurrence of carbonization during the decomposition process. The carbon formation has been observed from the mechanochemical decompositions of organic polymers such as polytetrafluoroethylene (PTFE)[22] and hexabromobenzene (HBB),[2] where hydrogen does not exist. In this case, although hydrogen exists in TCB, 6 h grinding operation also changes the TCB into amorphous carbon. The spectrum of 1 h ground sample exhibits a very high background. This may be attributed to the existence of organic compositions which function as the impurities to CaO to raise the fluorescence for Raman measurement. Prolonged grinding to 6 h results in a low and flattened baseline due to the less fluorescence, indicating that almost no organic impurities remain in the sample. Both results by Raman analysis and water-soluble chlorine measure-
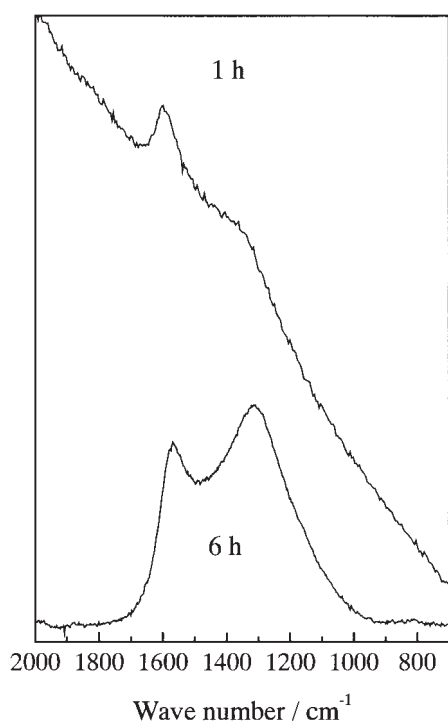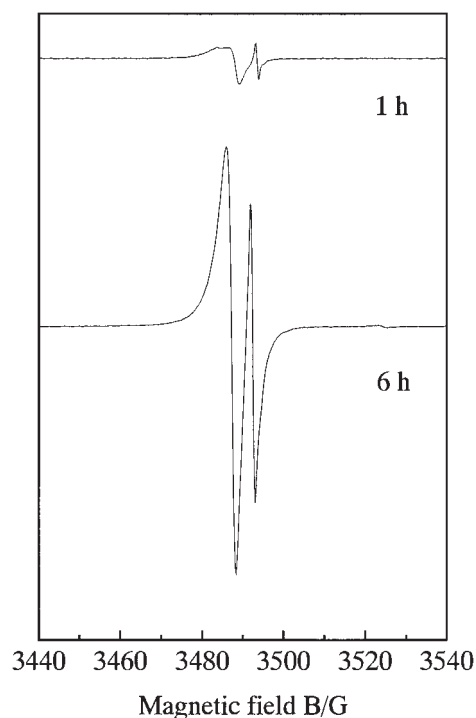

Fig. 6.   ESR spectra of 1 h and 6 h ground samples.

ment have shown that organic TCB has been mineralized completely by forming inorganic chloride and amorphous carbon.

Figure 6 shows the ESR spectra of the ground samples. Radical signals are clearly observed and their intensity increases with an increase in grinding time. Although detailed interpretation on the compositions of the radical needs further research work, the related information on the radicals formed in a similar way reported previously could be taken as references.[1,2,23] The broad peak around 3475–3500 B/G could be attributed to organic radicals and the sharp ones may result from the trapped free electrons inside inorganic oxide. The concentrations of both radicals rose up with the progress of grinding; especially the former became higher than the latter. It is supposed that radicals are induced by grinding on CaO surfaces and subsequently the charge transfer occurs to organic TCB. And C–Cl bonding in TCB tends to decompose to produce some intermediates or products. It can be said that the mechanochemical decomposition is related with the formation of radicals.

The above data have clearly shown that the decomposition of TCB is achieved by the mechanochemical reaction with CaO. Because various types of chlorinated compounds may be involved during the practical application of the mechanochemical process, a deeper understanding toward the decomposition mechanism is required in order to assure the effectiveness of the process to any type of compound. From the above data, it seems that the pathway of decomposition involves several possibilities. Here the problem is considered based on whether it is dechlorination or dehydrochlorination.

If the TCB sample is presumed to decompose mechanochemically through the dehydrochlorination pathway as follows:
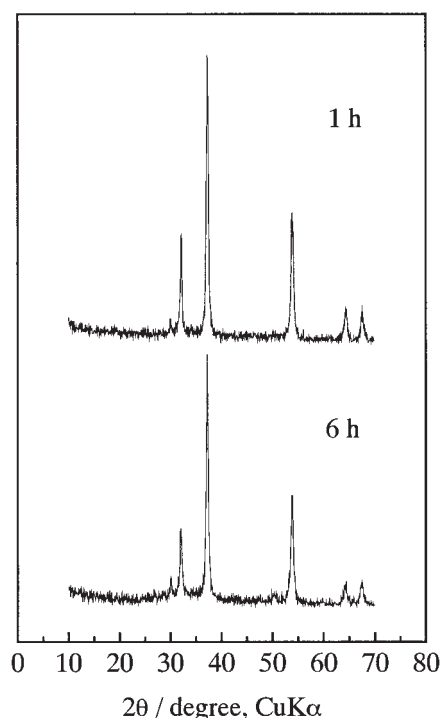

Fig. 5.   Raman spectra of the mixtures ground for 1 h and 6 h.

Fig. 7. XRD patterns of 1 h and 6 h ground samples.

$$C_6H_3Cl_3 + CaO \rightarrow C_6H_2Cl_2 + CaOHCl \quad (1)$$

$$C_6H_2Cl_2 + CaO \rightarrow C_6H_1Cl_1 + CaOHCl \quad (2)$$

$$C_6H_1Cl_1 + CaO \rightarrow 6C + CaOHCl \quad (3)$$

And three steps of dehydrochlorination may result in the formation of carbon, possibly explaining the reason for the carbon occurrence. In fact, the mechanochemical decomposition of poly(vinyl chloride) has been observed to occur through a dehydrochlorination pathway and the crystalline phase of CaOHCl has been detected in the ground sample.[24,25] However, the formation of crystalline CaOHCl here has not been observed from the XRD analysis results shown in Fig. 7, suggesting that the chloride formed is a amorphous one. In this case, XRD patterns show only CaO existence both in 1 h and 6 h ground samples. The peak intensity of 6 h ground sample is smaller than that of 1 h, indicating the progress of mechanochemical reaction and decomposition of TCB. The amorphous state of chloride can not offer direct information about products.

Taking together the analytical results, we can make some deductions about the compositions of the ground products. When Cl is separated from C, it tends to absorb CaO. On the other hand, the O of CaO tends to form combination with TCB, via hydrogen bonding for example. The exchange between the combination results in the Ca chloride and an organic phase consisting of C, H and O. Ca chloride has a strong tendency to absorb water to form a hydrate. On the other hand, the organic phase with C, H and O tends to dehydrate during grinding. As a result, Ca chloride hydrate and amorphous carbon are obtained as the most stable state through water exchange. It may be difficult to imagine such a water exchange between organic and inorganic compounds. In fact, if CaO and CaSO₄·2H₂O (gypsum) are ground together, water

exchange is induced mechanochemically to form Ca(OH)₂ and CaSO₄·0.5H₂O (gypsum hemihydrate), as is clear by phase identification. This can help one to understand why the state of chloride is amorphous and the formation of carbon occurs.

The existence of radicals also offers more evidence that dechlorination is more reasonable than dehydrochlorination. The dechlorination pathway means the separation of C–Cl bonding, leaving free radicals in the ground sample. The dehydrochlorination pathway implies that both C–Cl and C–H bondings are disconnected simultaneously to form HCl absorbed by CaO as CaOHCl and an intermediate phase with a structure similar to benzyne. This will leave less chance for the formation of free radicals.

Furthermore, based on the supposed dehydrochlorination pathway, it is difficult to interpret the formations of other intermediate phases such as TeCB, DCB, CB, toluene, benzene and gases with low molecular weight, such as H₂O, C₂H₆, CO₂, CH₄. The joint cut-off of chlorine and hydrogen from benzene ring leads to the possible intermediate phases of C₆H₂Cl₂ and C₆H₁Cl₁. The formations of the above compounds seem to support the notion of a separate dechlorination of Cl rather than the joint disconnection of H and Cl from the benzene ring. Therefore, a dechlorination pathway rather than a dehydrochlorination pathway is reasonable. This will be discussed again based on the following results from computational chemical simulations.

Simulation Part Based on Computer Chemistry. To confirm this experimental data, we used a semi-empirical molecular orbital method to simulate the TCB decomposition process. Due to the difficulty in calculating the direct bonding between Cl and Ca, the purpose of the calculation was focused on the difference in easiness of C–Cl separation from that of the joint separations of C–Cl and C–H to form HCl, without considering the effect of CaO existence.

Table 1 shows the "bond energy", "barrier energy" and "final energy" values of a 1,3,5-TCB model molecule. The bond energy is defined as the increasing internal molecular energy

Table 1. 1,3,5-Trichlorobenzene Internal Energy

	Bond energy /kJ mol⁻¹	Barrier energy /kJ mol⁻¹	Final energy /kJ mol⁻¹	Possibility products
C–C bond				
1C–2C	64	699	497	7 nucleus
2C–3C	64	699	497	7 nucleus
3C–4C	64	699	497	7 nucleus
4C–5C	64	699	497	7 nucleus
5C–6C	64	699	497	7 nucleus
6C–1C	64	699	497	7 nucleus
C–H bond				
1C–7H	44	—	771	
3C–9H	44	—	771	
5C–11C	44	—	771	
C–Cl bond				
2C–8Cl	29	—	558	
4C–10Cl	29	—	558	
6C–12Cl	29	—	558	

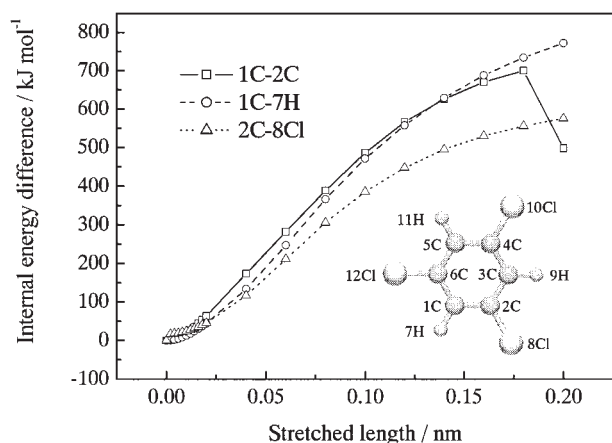1,3,5-TCB: original energy 16.3 kJ mol⁻¹.

Fig. 8. Internal energy in C–C, C–H and C–Cl bonds in the model molecule of 1,3,5-TCB calculated by the semi-empirical method as a function of the stretched length between neighboring elements.

when each bond distance (C–H, C–Cl and C–C) is stretched until 0.02 nm. The bond energy of C–Cl is 29 kJ mol^{-1}, which is the lowest one of all. This means that the C–Cl bond is the weakest bond, where the decomposition likely started. This simulation data also reveal that the decomposition is due to the dechlorination because the energy of C–H is higher than C–Cl. Furthermore, the 1,3,5-TCB model molecule has no chance to release HCl from the structure, even if chlorines in the 1,3,5-TCB model molecule are located at an ideal position. There is a chance for Cl, H or hydrocarbons to combine with another benzene to form TeCB, TCB, DCB and other chemicals. Figure 8 shows the bond energy for C–C, C–H and C–Cl in the 1,3,5-TCB model molecule as a function of stretched length. In general, the binding force between the two-neighbor elements is weak when the internal energy is low at the same stretched length. This means that the molecule is chemically unstable. The figure indicates that the C–Cl bond is located in the lowest side in the range of stretched length. This is very consistent with the experimental results shown in Figs. 1 and 2.

In contrast, Table 2 shows internal energy values of 1,2,3-TCB as a function of stretched length. Final energies of 1C–7H and 3C–9H are lower than barrier energies. This means that Cl may separate together with H to form HCl. When 7H and 9H are stretched continuously, HCl (consisting of 7H–12Cl, 9H–10Cl) can be formed at the long stretched length of around 0.18 nm. However, product energies of HCl are too big for practically forming HCl for the 1,2,3-TCB model molecule. Therefore, it is reasonable to say that the 1,2,3-TCB decomposition is caused by the release of Cl from the benzene ring structure of the molecule. Figure 9 shows calculated potential energy between each two neighboring elements, such as C–Cl, C–H and C–C in the model molecule of 1,2,3-TCB, as a function of the stretched length when extended by certain external force. It is also found from the figure that the C–Cl bond is the weakest one of all, implying that the decomposition starts from this bond in the model molecule.

Conclusions

Trichlorobenzene was ground in air with CaO by using a planetary ball mill to investigate the decomposition phenom-

Table 2. 1,2,3-Trichlorobenzene Internal Energy

	Bond energy /kJ mol^{-1}	Barrier energy /kJ mol^{-1}	Final energy /kJ mol^{-1}	Possibility products
C–C bond				
1C–2C	64	—	761	
2C–3C	64	751	251	
3C–4C	63	711	249	
4C–5C	63	592	390	7 nucleus
5C–6C	63	592	390	7 nucleus
6C–1C	63	—	745	
C–H bond				
1C–7H	44	771	380	HCl
3C–9H	44	771	764	
5C–11C	44	771	380	HCl
C–Cl bond				
2C–8Cl	29	—	564	
4C–10Cl	29	—	573	
6C–12Cl	29	—	564	

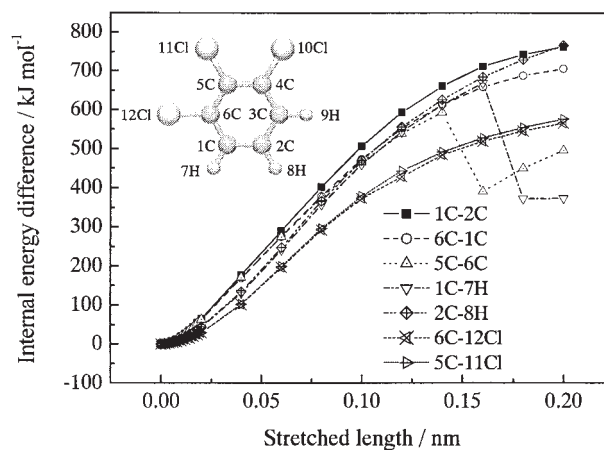1,3,5-TCB: original energy 23.6 kJ mol^{-1}.

Fig. 9. Internal energy in C–C, C–H and C–Cl bonds in the model molecule of 1,2,3-TCB calculated by the semi-empirical method as a function of the stretched length between neighboring elements.

ena experimentally. In addition, the simulation on the potential energy of each bond in the TCB model molecule was conducted based on the computational chemical simulation. The results are summarized as follows:

1) The TCB can be decomposed mechanochemically by the grinding with CaO through dechlorination, while is induced by the charge transfer generating radicals.

2) The final product is composed of Ca chloride hydrate and amorphous carbon, with minute amounts of several kinds of stable gases.

3) The simulation on the potential energy of the TCB model molecule reveals that the molecule is decomposed by dechlorination. This is consistent with the experimental result.

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