Enhanced Decomposition of Dichloromethane in Air by Multi-Pass Electron Beam Irradiation

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The decomposition of dichloromethane (CH_2Cl_2) in model air gases (concentration, around 100 ppm) by electron beam (EB) and γ-ray irradiation was studied using batch-type glass reactors of 500 ml volume. The addition effect of water on the decomposition was also investigated. In dry air, one-pass EB irradiation (10.7 kGy s^{-1}) induced only 65% decomposition, even at 32 kGy, but the γ-ray irradiation (2 kGy h^{-1}) or EB multi-pass irradiation (1.33 kGy s^{-1}) decomposed CH_2Cl_2 100% at 32 kGy. Water addition (4 ml) enhanced the decomposition percentage to 96% at 16 kGy, even by one-pass irradiation. In dry air, the formation of CO_2, CO, phosgene and chloroform was confirmed. The mechanism for the above addition effect was considered as well as for the multi-pass irradiation effect.

Dichloromethane (CH_2Cl_2) has been released from various industries to the atmosphere. Although activated carbon has been used for treating this off gas, but it requires high cost. Now, a more effective method is required. We have shown that electron beam (EB) irradiation is effective for the decomposition of volatile organic compounds (VOCs) in air.[1,2] High-energy electrons produce active species such as ions, secondary electrons, atoms, and free radicals in air. These active species contribute to the VOCs decomposition. Recently, Penetrante et al.[3] studied the dichloromethane decomposition in nitrogen and air by EB irradiation in a flow system. They showed that although dichloromethane could be efficiently decomposed in nitrogen, the decomposition percent was almost saturated at 70% in air, even by increasing the doses to more than 60 kGy. They did not study the effects of the dose rate, irradiation time or additives.

However, these parameters must influence the decomposition. Thus, in this study we investigated these effects on the decomposition, and found that dichloromethane decomposition in air is enhanced by multi-pass EB irradiation or by the addition of water.

Experimental

Materials. Pure air from Nippon Sanso Co., Ltd. was used as a base gas. The concentration of CO, CO_2, and CH_4 in this air is less than 1 ppm. Dichloromethane, 99.5% from Wako Chemical Co., Ltd. was used without further purification.

Preparation of Model Gas. Sample gases containing dichloromethane were prepared by bubbling the base gas through liquid dichloromethane. Gases containing dichloromethane were diluted with the base gas in a gas mixer and introduced into several reactors connected in series. The glass reactors were made from Pyrex glass, and had the external dimensions of approximately 50×50×200 mm, with two stop cocks at both sides. The change in the flow rates of bubbling gas and base gas adjusted the dichloromethane concentration in the sample gas. The concentration was measured with a gas chromatograph (Shimadzu GC-9AM) equipped with a packed column and flame ionization detection (FID). The dichloromethane concentration before irradiation was adjusted to be 60—200 ppm. After the concentration in the reactors was attained to be constant, the two cocks were closed. The water in the sample gases could not be completely removed. The water content, measured with a water meter, was 300—500 ppm.

Irradiation and Analyses. A 2 MeV electron accelerator was used for EB irradiation. All irradiations were carried out at room temperature. The average dose rate in the glass reactor was measured by a CTA film dosimeter (FTR-125, Fuji Photo Film Co., Ltd.).

The experiments were carried out in four ways. In the first, the glass reactors were put on a conveyor and passed under a scan horn of the electron accelerator with a conveyor speed of 1 m min^{-1} (one-pass irradiation). The total dose was adjusted to be 4—32 kGy by changing the beam current. In the second method, the glass reactors were passed several times under the scan horn at a conveyor speed of 1 m min^{-1} and a constant current (multi-pass irradiation). The total dose was adjusted by changing the pass times. In the third method, experiments were conducted with water addition (0.01—4 ml) in the reactors. For a comparison, in the fourth method, a plate-type Co-60 was used for γ-ray irradiation at ambient temperature. The dose rate in the glass reactor was 2 kGy h^{-1}.

After irradiation, a rubber stopper was put to one side of the glass reactor. The air between the rubber stopper and the cock was evacuated with a syringe. The cock was then opened, and 1.5 ml of

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the gas in the glass reactor was collected with a syringe through the rubber stopper for analyses. To measure carbon dioxide (CO_2), a Shimadzu TOC-5000 analyzer (total organic carbon analyzer) was used. Gas detectors made by Gastec Inc. were used to measure phosgene ($COCl_2$), carbon monoxide (CO), chlorine (Cl_2) and hydrogen chloride (HCl). An ion chromatograph was used to measure the chloride ion (Cl^-) concentration in the water recovered from the reactors.

Results and Discussion

Decomposition in Dry Air. Figure 1 shows the decomposition percentages of dichloromethane (CH_2Cl_2) to the initial concentration versus the doses by ionizing radiations (EB and γ-ray irradiation) in dry air. The EB dose rate was 1.33 kGy s^{-1} for multi-pass irradiation and 1.33—10.7 kGy s^{-1} for single-pass irradiation. By multi-pass irradiation, the decomposition percentage increased substantially with the dose, and CH_2Cl_2 was not detected at 32 kGy in the irradiated gas with the gas chromatograph, indicating that CH_2Cl_2 was decomposed almost 100%.

In contrast, by using single-pass irradiation, the maximum decomposition percentage was 65%, and it did not increase in the 16—32 kGy dose range. This result is in good agreement with that by Penetrante et al.,[3] who irradiated air containing 100 ppm of CH_2Cl_2 by EB in a flow system.

The time for the multi-pass irradiation was from 3 to 24 s (3 s for each pass). It appears that a longer irradiation time by EB with a small dose rate makes the decomposition more effective. This is also indicated by the results based on γ-ray irradiation, where the decomposition percentage by γ-rays increased more substantially than by the above-mentioned EB irradiation. The decomposition was completed at 32 kGy.

Decomposition in Humid Air. In humid air, OH radicals play an important role in the oxidation of SO_x and NO_x in a flue-gas treatment by EB (Mätzing,[4] Mätzing et al.[5]). We thus expected that water addition in the glass reactor might enhance the decomposition.

However, when we added water (0.01 ml) to the sample gas (500 ml), the decomposition percentage decreased drastically by 45%, as shown in Fig. 2. This is the result obtained by EB single-pass irradiation of 32 kGy with dose rates of 1.33—10.7 kGy s^{-1}. The added water (0.01 ml) completely vaporized in the reactor, leading to a water content of about 3% in the reactor. After this minimum point, the decomposition percentage increased again with the amount of added water. Any added water more than 0.05 ml remained as a liquid layer on the reactor wall. Thus, the liquid water on the reactor wall can be related to an increase in the decomposition percentage.

In order to find a more effective decomposition condition, we examined the effect of different volumes (0.1—4 ml) of water with a single-pass and a small dose rate (0.53 kGy s^{-1}) at 16 kGy. The result is shown in Fig. 3, indicating that the decomposition percentage increased with the volume of

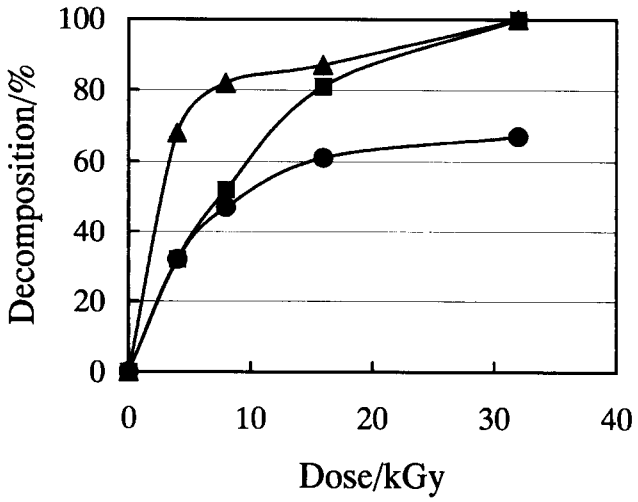

Fig. 1. The decomposition of dichloromethane (CH_2Cl_2) vs. doses by ionizing radiations in dry air. Electron beam (EB): one-pass irradiation (●); multi-pass irradiation (■); γ-rays (▲).

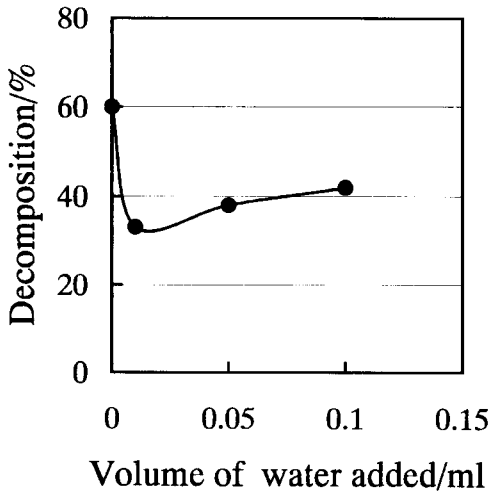

Fig. 2. Water addtion effect on the CH_2Cl_2 decomposition. EB one-pass irradiation of 32 kGy with a dose rates of 10.7 kGy s^{-1}.

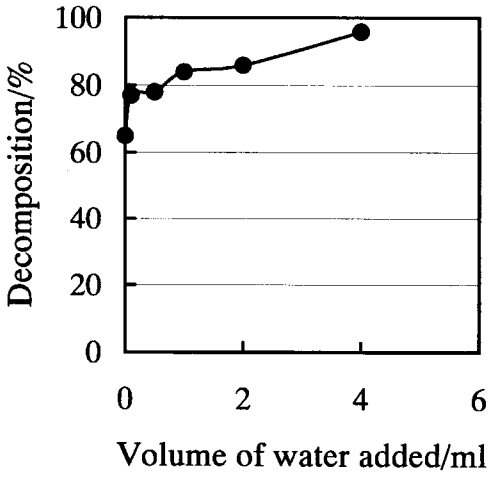

Fig. 3. Water addtion effect on the CH_2Cl_2 decomposition. EB one-pass irradiation of 16 kGy with a dose rate of 0.53 kGy s^{-1}.

added water. The maximum decomposition percentage was achieved at the addition of 4 ml, and the decomposition percentage became 96%. Figure 4 indicates the decomposition percentage versus to the doses with the addition of 4 ml water under the same irradiation condition as in Fig. 3. The decomposition percentage increased substantially by water addition, especially by 16 kGy, from 58 to 96%.

On the other hand, water can dissolve dichloromethane. We thus measured the amount of dicloromethane dissolved in the 4ml water added for a correction. The dichloromethane concentration decreased by only 2—3%, even two hours after the water injection. The time from the water injection to the dichloromethane measurement via EB irradiation was almost within two hours. Thus, the result from the present experiment required no correction.

By-Products. Figures 5 and 6 show the CO_2 concentration in the irradiated dry gases by single-pass EB irradiation (1.33—10.7 kGy s^{-1}) and by multi-pass EB irradiation (1.33 kGy s^{-1}) versus doses together with the remaining dichloromethane concentration, respectively. In the latter irradiation, the CO_2 concentration increased substantially to 72 ppm at 32 kGy, which corresponds to 55% of the decomposed dichloromethane. Multi-pass irradiation is preferable for the mineralization of dichloromethane.

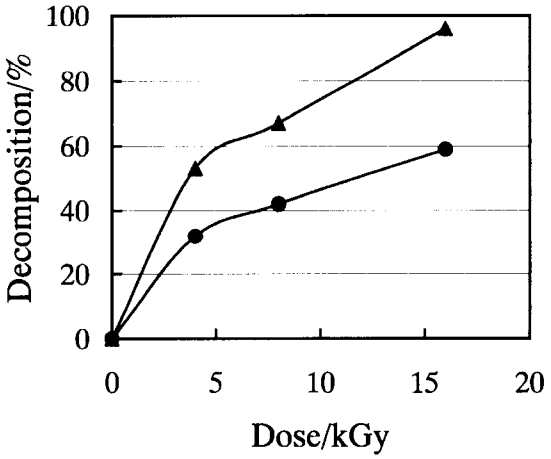

Fig. 4. CH_2Cl_2 decomposition vs. doses in dry air (●) and in the presence of 4 ml of water (▲). EB one-pass irradiation of 16 kGy with a dose rate of 0.53 kGy s^{-1}.

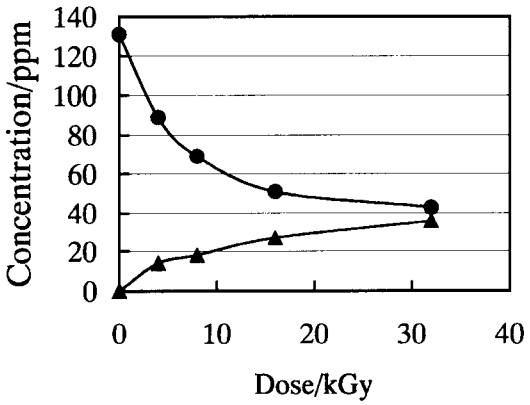

Fig. 5. CO_2 formation vs. dose from the CH_2Cl_2 decomposition in dry air. The remaining CH_2Cl_2 concn (●) and the CO_2 concn (▲). EB one-pass irradiation with dose rates of 1.33—10.7 kGy s^{-1}.

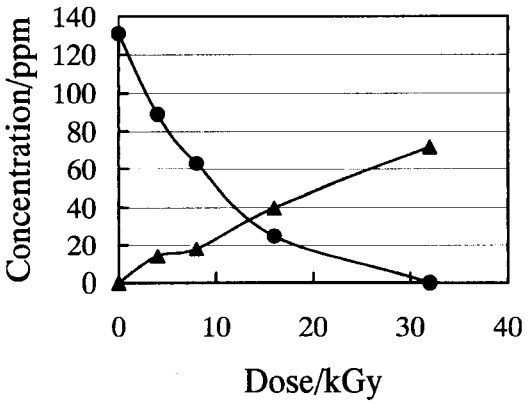

Fig. 6. CO_2 formation vs. dose from the CH_2Cl_2 decomposition in dry air. The remaining CH_2Cl_2 concn (●) and the CO_2 concn (▲). EB multi-pass irradiation with dose rates of 1.33 kGy s^{-1}.

We did not detect any carbon monoxide (CO) at 8 kGy, but at 16 and 32 kGy the CO concentration was about 3 and 11% of the decomposed dichloromethane, respectively, as shown in Fig. 7. This figure also shows the phosgene ($COCl_2$) concentration in the irradiated gass. The concentrations were around 10—15% of the decomposed dichloromethane.

The total carbon means the sum of the concentrations of CO_2, CO, $COCl_2$, and the remaining dichloromethane. The data in Fig. 7 indicate that the carbon losses were around 20% at 8 and 16 kGy and around 6% at 32 kGy. This result suggests that some intermediate products were produced at 8 and 16 kGy, and were deposited on the wall of the glass reactor.

We assumed that intermediate products are easy to be absorbed on the reactor wall. After irradiation, we injected 10 ml of water into the reactor, followed by shaking and leaving for 30 min. After that, we measured the Cl^- ions in the solution with an ion chromatograph. The Cl^- ion con-

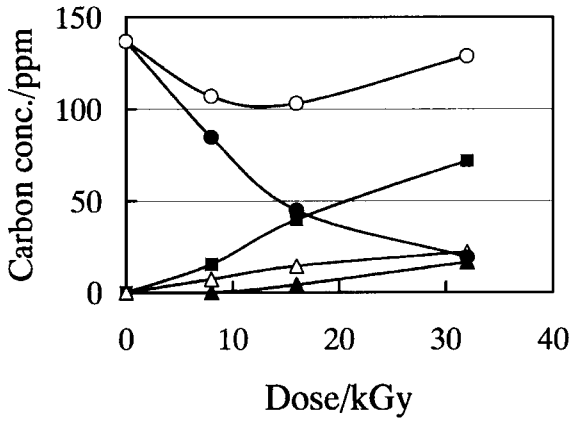

Fig. 7. Carbon balance vs. doses for the CH_2Cl_2 decomposition in dry air. The remaining CH_2Cl_2 concn (●), CO_2 (■), CO (▲), $COCl_2$ (△), and the summation of carbon (○). EB multi-pass irradiation with 1.33 kGy s^{-1}.

centration was shown in Fig. 8 together with the remaining dichloromethane concentration and the summation of total chlorine. It can be seen that the total chlorine recovery was around 100% at 4, 8, and 16 kGy, and about 80% at larger doses. This result also indicates that the intermediate products produced in the reactor were easily dissolved in water and decomposed to produce Cl^-. We did not detect Cl_2 with the gas detectors. We detected a small chloroform peak in the gas chromatogram, which corresponded to few ppm. In water-added sample gas, this peak was not observed.

G Values. The G value (given in $\mu mol\,J^{-1}$) is defined by the molecular yield per unit energy of absorption from the radiation. The values for the dichloromethane decomposition were calculated from the doses of 0—4 kGy, and are given in Table 1. The G values are around 0.31—0.42 $\mu mol\,J^{-1}$, indicating that the decomposition is not induced via chain reactions. The G values by γ-ray irradiation are about 1.5-times larger than those by single-pass EB irradiation with a dose rate of 1.33 $kGy\,s^{-1}$, and almost the same as that by single-pass EB irradiation with a dose rate of 0.53 $kGy\,s^{-1}$.

Decomposition Mechanism. EB irradiation of air produced nitrogen atoms, oxygen atoms, cations (N_2^+, N^+, O_2^+, and O^+), and secondary electrons. Their G values are estimated to be 0.254, 0.029, 0.189, 0.057, 0.043, 0.026, and 0.315 $\mu mol\,J^{-1}$, respectively.[6]

Among these species, the cations (N_2^+, N^+, O_2^+, and O^+) produced OH radicals by the following reactions in the presence of several hundred ppm of water:

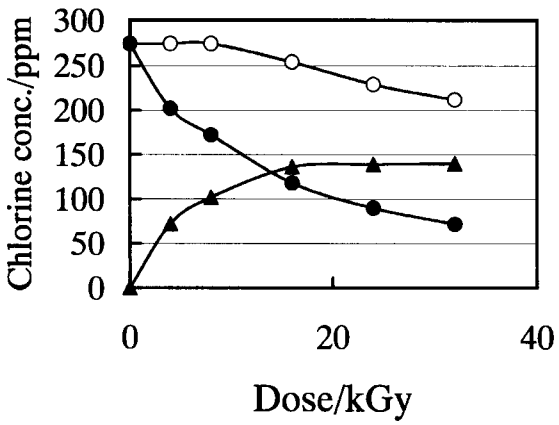

Fig. 8. Chlorine balance vs. doses for the CH_2Cl_2 decomposition in dry air. The remaining CH_2Cl_2 concn (●), Cl^- ion (▲), and the summation of chlorine (○). EB multi-pass irradiation with 1.33 $kGy\,s^{-1}$.

Table 1. The G Value of Dichloromethane Decomposition and the G Value of Inorganic Carbon (CO_2) Formation in Dry Air

Radiation	Dose rate	$G(CH_2Cl_2)$[a)]	$G(CO_2)$[a)]
Electron beam	1.33 $kGy\,s^{-1}$	0.30	0.12
	0.53 $kGy\,s^{-1}$	0.40	0.35
γ-Rays	2 $kGy\,h^{-1}$	0.45	0.17

a) In $\mu mol\,J^{-1}$.

$$N_2^+, N^+ + O_2 \rightarrow N_2, N + O_2^+, \quad (1)^7$$

$$O_2^+, O^+ + H_2O \rightarrow O_2, O + H_2O^+, \quad (2)^{6,8}$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH. \quad (3)^{6,8}$$

The G(OH) can be assumed to be 0.315 $\mu mol\,J^{-1}$. The OH radicals can react with dichloromethane (the rate coefficient: 1.4×10^{-13} molecule $cm^{-3}\,s^{-1}$),[9]

$$OH + CH_2Cl_2 \rightarrow H_2O + CHCl_2. \quad (4)$$

On the other hand, the secondary electrons attach to the background oxygen readily by the following reactions to produce O_2^- ions;[10]

$$e^- + O_2 + N_2, O_2 \rightarrow O_2^- + N_2, O_2. \quad (5)$$

The N_2 and O_2 molecules act as third bodies in Eq. 5. The secondary electrons also react with dichloromethane, but the rate coefficient is small (6.5×10^{-13} molecule $cm^{-3}\,s^{-1}$).[11] On the contrary, the O_2^- anions react with dichloromethane with a large rate coefficient (1.1×10^{-9} molecule $cm^{-3}\,s^{-1}$) to decompose it according to the following;[12]

$$O_2^- + CH_2Cl_2 \rightarrow O_2 + \text{products}. \quad (6)$$

The nitrogen atoms also contribute to the decomposition according to the next reaction;[13]

$$N + CH_2Cl_2 \rightarrow \text{products}. \quad (7)$$

Penetrante et al.[3] have proposed that reaction (7) is mainly responsible for the dichloromethane decomposition in nitrogen and air. As for the oxygen atoms, they react with dichloromethane only with very slow rates.[14]

From the above discussion, three active species (OH radicals, O_2^- anions and nitrogen atoms) have the possibilities to contribute to the dichloromethane decomposition in air containing several hundred ppm of water. We then simulated the decomposition based on the above reactions using a computer, and estimated their contributions to the decomposition. The result indicated that the contributions are nearly 40, 40, and 20% for OH radicals, O_2^- anions, and nitrogen atoms, respectively.

When we consider the decomposition mechanism, Fig. 2 is very suggestive, which indicates that the addition of 0.01 ml of water (corresponding to a water concentration of 3%) reduced the decomposition by 45%. This reduction cannot be explained by reaction (7), as proposed by Penetrante et al.[3]

On the other hand, O_2^- anions are clustered with water molecules in the presence of water, leading to produce $O_2(H_2O)^-$, $O_2(H_2O)_2^-$, and $O_2(H_2O)_3^-$.[15] The rate coefficients of these clustered ions to CF_2Cl_2 are 1/10—1/1000 for O_2^- anions.[15] This suggests that the reactivities of these clustered O_2^- anions to dichloromethane are much smaller than that for O_2^- anions.

Taking into account the above clustered O_2^- anions, the decomposition reduction in Fig. 2 can be clearly explained;

that is, in the presence of much water, almost all of O_2^- anions clustered with some water molecules can not contribute to the dichloromethane decomposition, resulting in a reduction by 45%. This reduction corresponds well to the above-mentioned simulation result.

The above discussion leads to the conclusion that the OH radicals, O_2^- anions and nitrogen atoms are responsible for the dichloromethane decomposition in air containing several hundred ppm of water, and that the former two species play the main roles. The contribution of O_2^- anions disappears in air containing much water.

Reaction Passes Leading to the By-Products. As previously described, the dichloromethane decomposition yields various by-products: CO, CO_2, $COCl_2$, and Cl^-. The reaction passes, leading to these products via some intermediates, which are considered to be similar to those proposed by Penetrante et al.,[3] Atkinson et al.,[9] and Sanhueza et al.[16]

Mechanism of Decomposition Enhancement by Water Addition. As shown in Fig. 2, the decomposition percentage increased with the addition of water up to more than 0.05 ml. This increase cannot be explained by the decomposition mechanism described above.

Dichloromethane decomposition yields various by-products and intermediates. As described in the previous section, some of them react with the active species responsible for the decomposition. For example, phosgene reacts with an electron very rapidly (a rate coefficient of 5×10^{-8} molecule cm^{-3} s^{-1}).[17] This also suggests that O_2^- anions react with phosgene rapidly to decompose it, just like in reaction (8). Thus, some of the by-products and intermediates act as strong scavengers of active species, resulting in decomposition reduction.

On the other hand, phosgene is dissolved in water. Water decomposes phosgene into CO_2 and HCl. Then, if a water layer exists on the reactor wall, the produced phosgene is dissolved in it without scavenging the active species. The other intermediates, such as COHCl and COCl, may also be dissolved in the water layer similarly. The dissolution of the produced phosgene and some intermediates without scavenging active species results in an enhancement of the dichloromethane decomposition, as shown in Fig. 2.

Mechanism of Multi-Pass Irradiation Effect. At a certain dose, the dichloromethane decomposition percentage by γ-ray irradiation and by multi-pass EB is higher than that by one-pass EB irradiation as shown in Fig. 1. This effect can also be explained by the deposition of the by-products or intermediates on the reactor wall, just like the above-mentioned-water addition effect. For example, in the case of γ-ray irradiation, it took almost 24 h. During the irradiation, phosgene or intermediates has much time to deposit on the reactor wall. Thus, the deposit of by-products and some intermediates on the reactor wall results in a decomposition enhancement.

Conclusion

The dichloromethane decomposition in model air gases was studied by the irradiation of an electron beam and γ-rays using a batch glass reactor of 500 ml volume. In dry air, dichloromethane was 100% decomposed at 32 kGy by electron-beam multi-pass irradiation (1.33 kGy s^{-1}) and γ-rays irradiation (2 kGy h^{-1}), respectively. The addition of water (4 ml) enhanced the decomposition. The products in dry air were CO_2, CO, $COCl_2$, HCl, and a 1—2 ppm of $CHCl_3$ (chloroform) at 32 kGy. The addition of a small amount of water or alkaline solution into the glass reactor after irradiation converted phosgene into CO_2 and HCl. This research has shown that dichloromethane in air can be easily decomposed by EB multi-pass irradiation or by adding water.

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