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Radiation-induced reactions *via* the lowest excited states in cinnamic acid crystals

Yasunari Maekawa,*[a] Tomonori Inaba,[b] Hiroki Hobo,[b] Tadashi Narita,[b] Hiroshi Koshikawa,[a] Seongyun Moon,[a] Jun Kato[a] and Masaru Yoshida[a]

[a] *Department of Material Development, Japan Atomic Energy Research Institute, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan. E-mail: yasum@taka.jaeri.go.jp*

[b] *Department of Materials Science and Engineering, Graduate School of Engineering, Saitama Institute of Technology, 1690 Fusaiji, Okabe, Saitama 369-0293, Japan*

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Radiation-induced reactions of cinnamic acid derivatives have been examined and compared with photoreactions in the crystalline state; all the reaction products were exactly the same as those of the photoreactions, indicating that the reactions proceed only *via* the lowest excited state to give [2 + 2] cycloadducts, *E*/*Z* isomerization products, or starting molecules.

Radiation-induced reactions by ionizing beams such as electron beams (EB) and ion beams, which can be focused on the nanometer scale and scanned at high speed, have recently attracted a great deal of attention as a promising technique for fabricating next generation electronic nano-devices as well as nano-lithography.[1] Radiation-induced reactions of saturated hydrocarbons have already been reported, and the mechanisms of ionization and excitation, as well as the subsequent radical or ionic reactions were described in detail.[2] In contrast, there have been few reports on rearrangement or C–C bond formation of organic molecules *via* radiation-induced ionization or excitation except for reports on simple compounds such as alkenes and stilbenes.[3] Chapiro *et al.* reported the mechanistic study for the radiolysis of diene and acenaphthylene crystals; however, these reactions proceeded with low conversion, along with a considerable amount of polymeric products.[4] Nevertheless, cinnamic acid crystals are known to undergo clean photoreactions such as [2 + 2] cycloaddition and *E*/*Z* isomerization between two olefinic double bonds; these reactions proceed without obvious side reactions by virtue of crystalline lattice restrictions.[5] Therefore, we applied this restricted matrix system for EB-induced reactions, which in general lead to many products in complex mechanisms.[6] Three cinnamic acids, which showed disparate photochemical behavior, were employed in order to reveal the reaction mechanism of radiation-induced reactions by comparison with the corresponding photochemical reactions.

Crystals of *E*-cinnamic acid (***E*1**) and *Z*-*o*-methoxycinnamic acid (***Z*2**) were obtained by recrystallization from ethanol. The salt crystal of ***E*1** and (±)-1-phenylethylamine with a 1 : 1 molar ratio was prepared by recrystallization from an ethanol solution of ***E*1** with an equimolar amount of (±)-1-phenylethylamine. Finely powdered crystals (*ca.* 0.07 g) were charged into a hollow of a glass plate with 1 mm depth and 10 mm diameter. The samples, which were covered with a Kapton™ film (12 μm thickness) and placed on the water-cooled copper metal plates, were irradiated with an EB of 1 MeV and 0.5 mA using a Cascade Type Electron Accelerator (Dynamitron).

An α-type crystal of ***E*1** was obtained by recrystallization from ethanol and was irradiated with doses of 1–20 MGy (0.56–11 mC cm^{-2}). The conversion and the products of the EB-induced reactions were analyzed by ^{1}H NMR spectroscopy. With an irradiation dose of 5 MGy, the olefinic peaks of ***E*1** at 6.6 and 7.6 ppm decreased with new increasing peaks at 3.8 and 4.3 ppm, which were attributed to the cyclobutane protons of centrosymmetric α-truxillic acid (***E*1**-dimer) by comparison with the photoproduct of ***E*1**.[7] As shown in Fig. 1, the relative concentration of the product, ***E*1**-dimer, reached its maximum value of 58% with 5 MGy, then gradually decreased to 17% with ***E*1** conversion of 86% at 20 MGy. The change in the X-ray diffraction patterns of the crystals during EB irradiation indicates that crystallinity was maintained with 5 MGy, but gradually deteriorated with further irradiation. Accordingly, EB irradiation of ***E*1** induces a [2 + 2] cycloaddition reaction under crystal lattice control with a dose of up to 5 MGy to give ***E*1**-dimer as the sole product in a yield of 58% (Scheme 1).

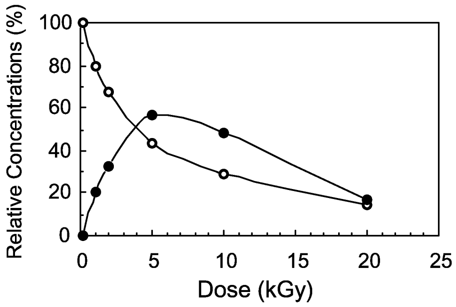
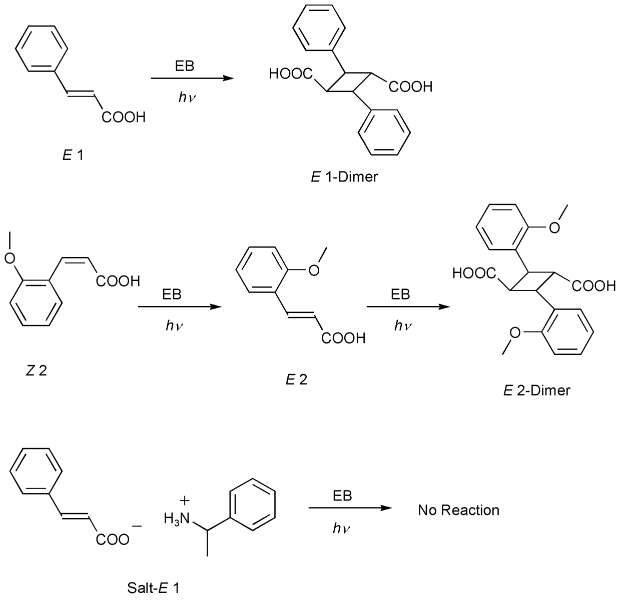


Fig. 1 The relative concentration of ***E*1** (○) and ***E*1**-dimer (●) plotted as a function of EB dose irradiating an ***E*1** crystal.

Z*2** Crystals obtained by recrystallization from a mixture of benzene and hexane also showed EB reactivity. With an irradiation dose of 10 MGy, the olefinic peaks of ***Z*2** at 5.9 and 7.0 ppm shifted to new olefinic peaks at 6.5 and 7.8 ppm, respectively. Since these peaks can be assigned to the olefinic protons of the *E*-isomer of ***Z*2** (E*2**) by comparison with the photoproduct of ***Z*2**, it is clear that EB irradiation induced *Z*/E



Scheme 1

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isomerization of ***Z*2** with a conversion of 61%.[8] Although ***Z*2** decreased with further irradiation and was quantitatively consumed with a dose of 20 MGy, the relative concentration of ***E*2** remained essentially constant (Fig. 2). On the other hand, a centrosymmetric dimer (***E*2**-dimer), which was also characterized from the cyclobutane proton appearing at 4.4 ppm in the ^{1}H NMR spectra by comparison with the photoproducts of ***Z*2** crystal, appeared with an irradiation dose of >15 MGy and reached a relative concentration of 28% at 20 MGy. A continuous change of X-ray diffraction patterns was observed with a slight deformation of the crystal during irradiation. Thus, EB irradiation of ***Z*2** induces *Z*/*E* isomerization to give ***E*2**, which in subsequent [2 + 2] cycloaddition yields ***E*2**-dimer under crystal lattice control. Note that the behavior observed during EB-induced reaction of ***E*2** crystals is exactly the same as the corresponding photoreaction behavior, which was reported by Schmidt *et al.*

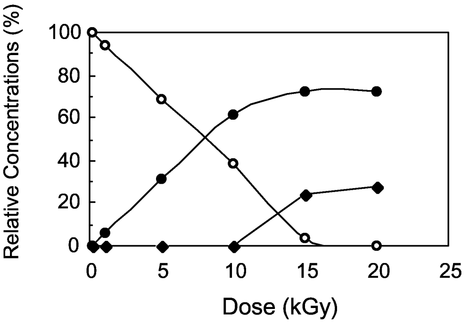

Fig. 2 The relative concentration of ***Z*2** (○), ***E*2** (●) and ***E*2**-dimer (◆), plotted as a function of EB dose irradiating a ***Z*2** crystal.

In contrast to the EB-induced reactions of ***E*1** and ***Z*2** crystals, a salt of ***E*1** and (±)-1-phenylethylamine with a 1 : 1 molar ratio (Salt-***E*1**) were stable upon EB-irradiation with doses of up to 10 MGy. This stability of the Salt-***E*1** with regard to EB is also the same as found for Salt-***E*1** upon UV irradiation.[9]

These EB-induced reactions, which give rise to the same products as those of the corresponding photoreactions, can be formulated by a mechanism in which all EB-induced reactions proceed *via* the lowest excited state, as is the case of photoreactions of cinnamic acid derivatives upon UV irradiation.[10] Fig. 3 shows a schematic energy diagram of EB-induced reactions of cinnamic acid crystals to compare with the corresponding photoreactions. The EB induced reactions are as follows: (1) radiolysis of molecules in the ground state (CA) leads primarily to upper exited states of CA (CA**) by direct excitation or to dissociation into a CA radical cation (CA$^{+\bullet}$) and a free electron, which subsequently recombine within picoseconds, resulting in the same CA**.[2,11] (2) The CA molecules in an upper excited state quickly relax to the lowest excited states (CA*), which is the same state as that introduced by photoexcitation. (3) From their lowest excited states, *E*-CA (***E*1** and ***E*2**) and *Z*-CA (***Z*2**) undergo [2 + 2] cycloaddition and *Z*/*E* isomerization, respectively; in contrast, CA Salt (Salt-***E*1**) reverts to a ground state by thermal relaxation. Both excited singlet and triplet states of CA derivatives are assumed to be involved in the course of the above EB-induced reactions since it is well known that [2 + 2] photocycloaddition and *Z*/*E* isomerization of CA derivatives proceed *via* the lowest singlet and triplet states, respectively.[12] Although we have not examined other radiation sources such as γ- and X-rays for the above reactions, the proposed mechanism should also be applicable because the energy diagram of the reactions include excited states and radical cations that are common reactive species in radiation-induced reactions.[1,2]

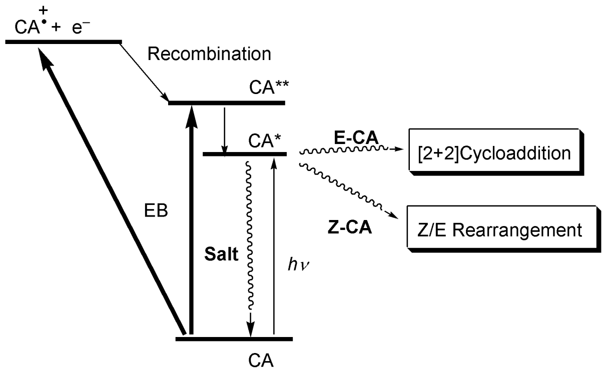

Fig. 3 A schematic energy diagram of EB-induced reactions of cinnamic acid crystals with the corresponding photoreactions. CA, CA*, CA** and CA$^{+\bullet}$ represent the ground state, the lowest excited state, an upper exited state, and radical cation of cinnamic acid derivatives (***E*1**, ***Z*2**, and Salt-***E*1**), respectively.

In conclusion, EB-induced reactions of cinnamic acid crystals are confirmed to proceed *via* the lowest excited state to give [2 + 2] cycloaddition and *Z*/*E* isomerization products. It should be stressed that the series of EB-induced reactions of CA derivatives is the first clear example to show exactly the same behavior as those of the corresponding photoreactions. This study has provided a preliminary view of the types of radiation-induced excited state reactions for olefinic molecules. Further studies are currently underway in the spectral analysis of these excited states as well as in exploring other EB-induced reactions.

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