A Novel Electron Beam-Induced Reaction of Sulfonium Salt in the Crystalline State

Seongyun Moon, Yasunari Maekawa,* and Masaru Yoshida
Department of Material Development, Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, 1233 Watanuki, Takasaki, Gunma 370-1292

(Received February 1, 2001; CL-010094)

The electron beam irradiation of triphenylsulfonium methanesulfonate in the crystalline state provides a new benzene-substituted sulfonium salt. This product has not been observed either by photolysis in the crystalline state nor by electron beam irradiation in a solution. The formation of the substitution product was confirmed by GC–MS analysis.

The electron beam resist system[1] has attracted great attention as a candidate for future lithography with its high resolving capacity, as compared with optical lithography which has resolution limitation due to its wavelength. High sensitivity in photoresists can be achieved by the incorporation of a chemical amplification concept, in which a photoacid generator (PAG), such as onium salts, decomposes to yield strong acids which amplify photochemical reactions, into the resist systems.[2] However, the current sensitivity and resolution are not sufficient for electron beam lithography, because onium salts were optimized for optical sources such as a UV light or an excimer laser. From such a point of view, it is important to explore organic compounds that are highly susceptible to electron beams to develop high performance electron beam resists.

There have been some reports about electron beam reactions of sulfonium salts in solutions.[3] In the solution, sulfonium salts react with the radical cations of the solvents ionized by electron beams to generate phenyl radicals as an intermediate species; however, the final products are the same as those in photolysis (Scheme 1).[4] Though the matrix (solvents or polymers) effect is considered to be an important characteristic for such electron beam reactions, no studies have been reported for sulfonium salts in the crystalline state. Therefore, we performed electron beam reactions of triphenylsulfonium methanesulfonate **1** in the crystalline state to investigate the mechanism of sulfonium salts that are directly ionized by the electron beam.

The introduction of methanesulfonate into the anionic moiety of sulfonium salt enables us to analyze the structure of radiolytic products by ^{1}H and ^{13}C NMR. The salt **1** having methanesulfonate as the anion was synthesized by condensation of diphenyl sulfoxide with benzene in the presence of phosphorus pentoxide in methanesulfonic acid at 65–70 °C for 12 h.[5] Pale yellow crystals were obtained in a yield of 57%.[6,7] Finely powdered crystals of **1** (0.07 g) were charged into a hollow of a glass plate which was 10 mm in diameter and 1 mm in thickness. The samples, which were covered with a Kapton film (thickness of 12 μm) and placed on the water-cooled copper metal plates, were irradiated using a Takasaki Electron Accelerator No. 2 (1 MeV, 0.5 mA) in an atmosphere of argon or air.

The progress of the electron beam reactions of **1** in the crystalline state was monitored by high performance liquid chromatography (HPLC), as shown in Figure 1.[7] When the sulfonium salt **1** was irradiated with an irradiation dose of 752 μC/cm^2 under argon gas, five major peaks appeared in the chromatogram (Figure 1a). Four of the products were assigned to be the same products as those by photolysis according to the following analytical procedures (Scheme 1).[4] The five major peaks were separated from one another by a reverse-phase preparative HPLC.[7] Two peaks at 7.7 and 13.6 min were assigned to diphenyl sulfide **2** and 4-(phenylthio)biphenyl **5** by comparing the retention time with authentic compounds, together with ^{1}H and ^{13}C NMR spectra. Two peaks at 10.7 and 13.3 min were assigned to ortho- and meta- isomers of **5**, 2-(phenylthio)biphenyl **3** and 3-(phenylthio)biphenyl **4** because both peaks showed the same parent peaks (*m/z* 262) and mass fragment patterns as **5** in MS spectra, and further, their ^{1}H and ^{13}C NMR showed spectra equivalent to data from the previous literature.[4]

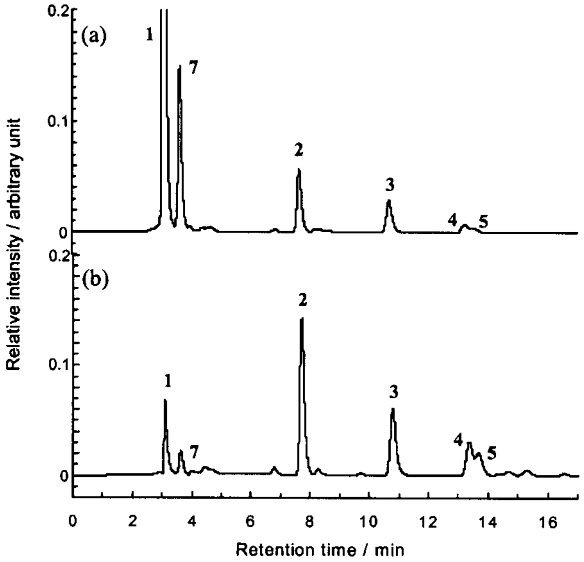
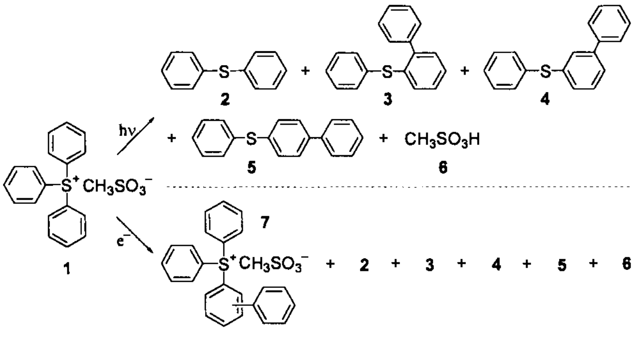


Figure 1. High-performance liquid chromatograms of **1** in the crystalline state irradiated with electron beams. (a) 752 μC/cm^2, (b) 2690 μC/cm^2.



Scheme 1. Products of electron beam-induced reaction of **1**.

The peak at 3.6 min in the chromatogram is the only product that has not been observed either by photolysis in the crystalline state nor by electron beam-induced reactions in the solution.[3,4] This new product exhibited similar properties to **1**, judging from similar HPLC retention times to each other in pure acetonitrile and aqueous acetonitrile eluents, and similar UV spectra with a broad triplet B-band at 233, 268 and 276 nm (λ_{max} = 233 nm). From these similarities, the new product should include a sulfonium salt form such as **1**. As shown in Figure 1b, the new product decomposed with 2690 μC/cm^2 along with an increase of the other four products; that is, this new product was accumulated as an intermediate product at an early stage, and then it gradually decomposed to the final products. Methanesulfonic acid **6** appeared at δ 2.72 (H of methyl) and δ 39.54 ppm (C of methyl) in ^{1}H and ^{13}C NMR spectra (in CD_3OD) when **1** and the new product decomposed in nearly quantitative yields (> 97%) with an irradiation dose of 2690 μC/cm^2. Accordingly, all the methanesulfonate anions are converted to **6** as a sole sulfonic product.

We performed gas chromatography–mass spectrometry (GC–MS) analysis of the new product to reveal its chemical structure. The new product showed a large peak (68.7%) at retention time of 16.38 min and two small peaks (9.6 and 21.7%) at 14.95 and 16.94 min on the basis of the ratio of each peak area in a gas chromatogram; these peaks exhibited the same fragment patterns with a base peak at *m/z* 262 in mass chromatograms (EI method).[8] As can be seen in Table 1, several sulfonium salts such as **1** and diphenyl-4-methoxyphenylsulfonium methanesulfonate **8** showed the base peaks which correspond to the mass number of the cationic structure subtracted by a phenyl group ($M - CH_3SO_3 - C_6H_5$). Therefore, from the GC–MS analysis of the sulfonium salts, the new product with a base peak at *m/z* 262 is assigned to be three regio-isomers of a benzene-substituted sulfonium salt, 2-, 3-, and 4-biphenyldiphenylsulfonium methanesulfonates **7** (Scheme 1). Furthermore, MS analysis of the new product using isobutane as a reagent gas (CI method) revealed the presence of the apparent peak at *m/z* 339 corresponding to the mass number ($M - CH_3SO_3$) of the cationic structure of the new salt.

Table 1. The assignment of base peaks in mass spectra

Samples	Base Peak	*m/z*
New Product	$M - CH_3SO_3 - C_6H_5$	262
1[a]		186
8[b]		216

[a]Triphenylsulfonium methanesulfonate. [b]Diphenyl-4-methoxyphenylsulfonium methanesulfonate.

The generation of a new benzene-substituted sulfonium salt **7** was not influenced by the presence of oxygen in the air because the amounts of the new salt **7** at each exposure dose based on the peak areas in the HPLC profiles were analogous under air and argon gas. Since the product **7** is not observed by the photolysis in the crystalline state,[4] the formation of the new salt may be due to the nature of the electron beam-induced reactions. At the present, the following mechanism may be considered for the formation of a new substitution product **7**; the electron beam irradiation induces ionization of **1** to generate sulfonium radical cations, which in subsequence, yield the new product through the coupling reaction with phenyl radicals. Further studies on the detailed mechanism are currently in progress.

References and Notes

1 N. Hirakawa, T. Tokuda, H. Aoki, Y. Nagasaki, and M. Kato, *J. Photopolym. Sci. Technol.*, **12**, 365 (1999); Y. Nagasaki, Y. Sato, M. Kato, H. Aoki, and T. Tokuda, *J. Photopolym. Sci. Technol.*, **12**, 369 (1999); T. Sakamizu, T. Arai, K. Katoh, S. Uchino, F. Murai, Y. Suzuki, and H. Shiraishi, *J. Photopolym. Sci. Technol.*, **11**, 547 (1998); T. Kozawa, S. Nagahara, Y. Yoshida, S. Tagawa, T. Watanabe, and Y. Yamashita, *J. Vac. Sci. Technol., B*, **15**, 2582 (1997).

2 H. Ito and C. G. Willson, *Polym. Eng. Sci.*, **23**, 1012 (1983); S. A. MacDonald, H. Ito, and C. G. Willson, *Microelectron. Eng.*, **1**, 269 (1983); Y. Maekawa, T. Miwa, Y. Okabe, G. Rames-Langlade, and T. Ueno, *Macromol. Rapid Commun.*, **21**, 35 (2000); N. Hayashi, T. Ueno, M. Hesp, M. Toriumi, and T. Iwayanagi, *Polymer*, **33**, 1583 (1992); H. Ito and M. Ueda, *Macromolecules*, **23**, 2885 (1990); J. M. J. Frechet, T. G. Tessier, C. G. Willson, and H. Ito, *Macromolecules*, **18**, 317 (1985); J. M. J. Frechet, S. Matuszczak, B. Reck, T. G. Tessier, H. D. H. Stover, and C. G. Willson, *Macromolecules*, **24**, 1746 (1991).

3 Y. Yamamoto, D. Werst, A. D. Trifunac, and S. Tagawa, 42nd Radiation Chemistry Conference of the Radiation Chemistry Society of Japan, Hiroshima, September 1999, Abstr., 11; S. Tsuji, T. Kozawa, Y. Yamamoto, and S. Tagawa, 42nd Radiation Chemistry Conference of the Radiation Chemistry Society of Japan, Hiroshima, September 1999, Abstr., 189; M. Wakita, S. Nagahara, Y. Yamamoto, and S. Tagawa, 42nd Radiation Chemistry Conference of the Radiation Chemistry Society of Japan, Hiroshima, September 1999, Abstr., 125.

4 J. L. Dektar and N. P. Hacker, *J. Am. Chem. Soc.*, **112**, 6004 (1990); N. P. Hacker, D. V. Leff, and J. L. Dektar, *Mol. Cryst. Liq. Cryst.*, **183**, 505 (1990); N. P. Hacker and K. M. Welsh, *Macromolecules*, **24**, 2137 (1991).

5 S. R. Akhtar, J. V. Crivello, and J. L. Lee, *J. Org. Chem.*, **55**, 4222 (1990).

6 ^{1}H NMR (270 MHz, CD_3OD), δ (ppm): 2.67 (s, 3H, methyl), 7.75–7.91 (m, 15H, benzene). ^{13}C NMR (68 MHz, CD_3OD), δ (ppm): 39.47, 126.21, 132.23, 132.26, 135.73. Purity (HPLC): 99.4% at the retention time of 3.1 min.

7 The HPLC system is composed of a pump (Hitachi, L7100), a UV detector (Hitachi, L7400, operated at λ = 235 nm), and a column (Showa Denko, Shodex ODSpak F511, packed with 5 μm octadecyl-bonded siloxanes). The eluent passing the column at 40 °C with a flow rate of 1 mL/min was a mixture of 10 mL pH 2 buffer solution, 20 mL H_2O and 90 mL acetonitrile.

8 MS (EI, *m/z*): 262 ($M - CH_3SO_3 - C_6H_5$), 186 ($M - CH_3SO_3 - C_6H_4C_6H_5$), 185 ($M - CH_3SO_3 - 2 \times C_6H_5$), 153 ($M - CH_3SO_3 - C_6H_5SC_6H_5$), 109 ($M - CH_3SO_3 - C_6H_5 - C_6H_4C_6H_5$).