

SELECTIVE FORMOSE REACTION INITIATED BY PHOTO- AND  $\gamma$ -IRRADIATION

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A selective formose synthesis was achieved by photo- and  $\gamma$ -irradiation of formaldehyde in the presence of base. Photoirradiation of aqueous formaldehyde solution gave pentaerythritol as a single product, while  $\gamma$ -irradiation resulted in the formation of glycolaldehyde as the main product. These results suggest that the formose reaction under photo- and  $\gamma$ -irradiation is considerably different from the thermal formose reaction.

Formose reaction has been attracting much attention recently from the view points of industrial manufacture of edible carbohydrates, as well as of the prebiotic synthesis of carbohydrates as a fundamental process of chemical evolution.<sup>1-4)</sup> The formose synthesis by catalysts, in general, results in complex products, e. g., the synthesis catalyzed by calcium hydroxide gives a mixture of more than 30 products.<sup>5)</sup> It is of particular interest in connection with practical use of the reaction to improve the selectivity and the yield.

Although much effort has been paid to improve the selectivity and the yield, the study is limited to the synthesis by organic and inorganic catalysts.<sup>6-12)</sup> Little is known about the selective formose synthesis by photo-<sup>13)</sup> and  $\gamma$ -irradiation. This paper reports highly selective productions of pentaerythritol by photoirradiation and of glycolaldehyde by  $\gamma$ -irradiation in the presence of bases.

Aqueous formaldehyde solutions ( $6.7 \text{ mol dm}^{-3}$ ) were bubbled with helium for 30 min prior to irradiation. Irradiation was carried out with a Xenon lamp (USHIO 500W,  $\lambda > 250 \text{ nm}$ ) or  $^{60}\text{Co}$   $\gamma$ -rays (dose rate  $7 \times 10^5 \text{ rad/h}$ ). The formaldehyde consumption was measured by a liquid chromatography.<sup>14)</sup>

After the reaction, the reaction mixture was neutralized hydrochloric acid, treated with ion exchange resins (IR-120 B and IRA-410). Then the effluent was evaporated to dryness at 45 °C under reduced pressure, giving formose mixtures which were subjected to gas chromatography after trimethylsilylation by the method of the literature.<sup>15)</sup>

Aqueous formaldehyde solution (6.7 mol dm<sup>-3</sup>) was irradiated in the presence of 0.31 mol dm<sup>-3</sup> of sodium hydroxide with light of longer wavelength than 250 nm for 3 h at 25 °C. Conversion of formaldehyde to the products was 37%. Figure 1 shows the gas chromatogram of the trimethylsilyl (TMS) derivatives of the formose mixture. A single product selectively formed was found at retention time of 21 min. The intensity ratio of the strong peak among the all products was higher than 96%.<sup>16)</sup> This product was identified as TMS derivative of pentaerythritol by direct comparisons of the gas chromatogram, the mass spectrum, and the <sup>13</sup>C-NMR spectrum with those of the authentic compound.

at this temperature (25 °C) any consumption of formaldehyde was not observed in the dark. Moreover, photoirradiation did not induce any consumption of formaldehyde in the absence of sodium hydroxide. Both sodium hydroxide and photoirradiation were necessary to get the selective reaction product.

Shigemasa et al.<sup>13)</sup> also reported that under UV irradiation in the presence of sodium carbonate pentaerythritol and 2-hydroxymethylglycerol are obtained from aqueous formaldehyde solution as the main products. The discrepancy with the present result is possibly due to the difference of the catalyst and irradiation conditions. The effect of base and irradiation conditions on the product distribution is currently under way.

As observed by photoirradiation, selective formose synthesis is also

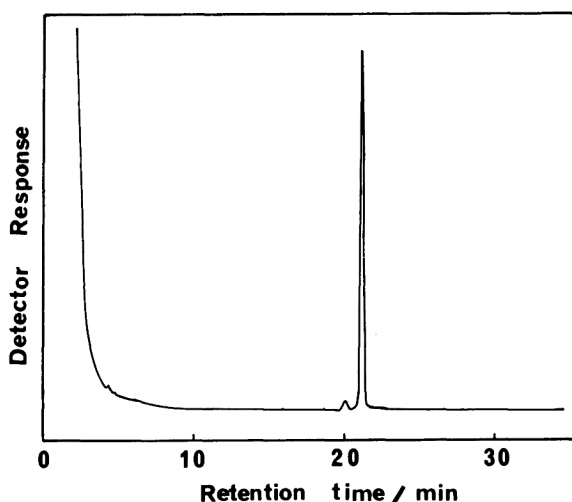


Fig. 1. The gas chromatogram of the TMS derivative of the product obtained by photoirradiation for 3 h in the presence of sodium hydroxide at 25 °C.

expected by  $\gamma$ -irradiation. An aqueous formaldehyde solution was irradiated with a total dose of  $4.2 \times 10^6$  rads in the presence of sodium hydroxide at  $25^\circ\text{C}$ . The gas chromatogram of the formose mixture after trimethylsilylation gave 6 peaks having almost similar intensities. The selectivity was not so good as compared with photoirradiation, though much better than the selectivity of the thermal reaction catalyzed by calcium hydroxide.<sup>5)</sup> To improve the selectivity, sodium hydroxide was replaced with molecular sieves.

A formaldehyde solution containing molecular sieves 4 A (25 vol%) was irradiated with a total dose of  $4.2 \times 10^6$  rads at  $4^\circ\text{C}$ . Conversion of formaldehyde to the products was 32%. The formose mixture was separated to two parts. One part was subjected to trimethylsilylation and the product was measured by a gas chromatography. The chromatogram gave a single peak, the retention time and the mass spectrum of which were identical to those of the TMS derivative of authentic glycolaldehyde. These results indicated selective formation of one product corresponding to glycolaldehyde. The formation of glycolaldehyde was also confirmed by a liquid chromatography combined with UV monitor, by which the yield was determined to be 24 mol%.

The other part of the formose mixture was reduced with sodium borohydride at room temperature and then subjected to trimethylsilylation. Figure 2 shows the gas chromatogram

of the trimethylsilylated products. The retention time of peak 1 was identical to that of TMS derivative of ethylene glycol. It is inferred from these results that a single product, glycolaldehyde, can be obtained by  $\gamma$ -irradiation in the presence of molecular sieves.

At the moment there is no convincing explanation for these selective formose formation. I am undertaking a search of other types of photo- and  $\gamma$ -initiated

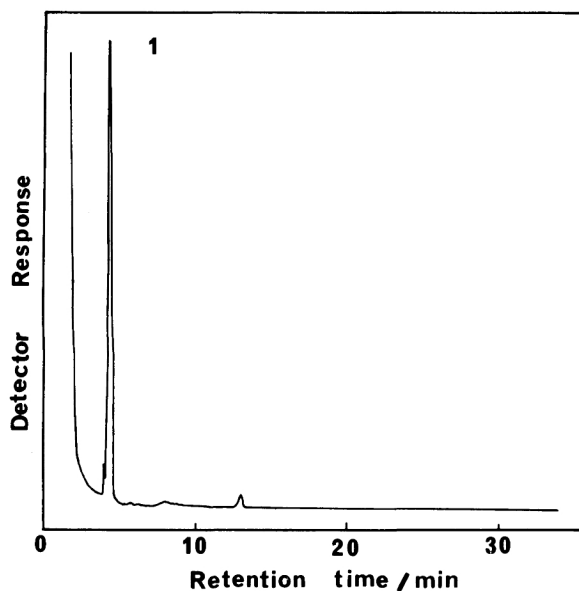


Fig. 2. The gas chromatogram of the TMS derivative of reduced product obtained by  $\gamma$ -irradiation in the presence of molecular sieves at  $4^\circ\text{C}$ .

formose reaction to clarify the mechanism.

The author is indebted to Dr. K. Shibata, Faculty of Science, Osaka City University for  $^{13}\text{C}$ -NMR spectral measurement.

#### References

- 1) T. Mizuno and A. H. Weiss, *Adv. Carbohydr. Chem. Biochem.*, 29, 173 (1974).
- 2) Y. Shigemasa, *Yuki Gosei Kagaku Kyokai Shi*, 36, 667 (1978).
- 3) M. Goto and T. Sakai, *Yuki Gosei Kagaku Kyokai Shi*, 41, 588 (1983).
- 4) T. Matsumoto and S. Inoue, *Kagaku*, 37, 49 (1982).
- 5) Y. Shigemasa, M. Kawahara, C. Sakazawa, and R. Nakashima, *J. Catal.*, 62, 107 (1980).
- 6) T. Matsumoto, M. Komiyama, and S. Inoue, *Chem. Lett.*, 1980, 839.
- 7) T. Matsumoto and S. Inoue, *J. Chem. Soc., Perkin Trans.*, 1, 1982, 1975.
- 8) T. Matsumoto and S. Inoue, *J. Chem. Soc., Chem. Commun.*, 1983, 171.
- 9) Y. Shigemasa, O. Nakae, C. Sakazawa, R. Nakashima, and T. Matsuura, *J. Am. Chem. Soc.*, 100, 1309 (1978).
- 10) Y. Shigemasa, T. Hamada, M. Hirabayashi, E. Waki, R. Nakashima, K. Harada, N. Kakeda, and M. Suzuki, *Chem. Lett.*, 1981, 899.
- 11) V. A. Likholobov, A. H. Weiss, and M. M. Sakharov, *React. Kin. Catal. Lett.*, 8, 155 (1978).
- 12) R. F. Socha, A. H. Weiss, and M. M. Sakharov, *J. Catal.*, 67, 207 (1981).
- 13) Y. Shigemasa, Y. Matsuda, C. Sakazawa, and T. Matsuura, *Bull. Chem. Soc. Jpn.*, 50, 222 (1977).
- 14) T. Sakai, M. Ishizaki, K. Kobayashi, and M. Goto, *Bull. Chem. Soc. Jpn.*, 54, 2083 (1981).
- 15) C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Am. Chem. Soc.*, 85, 2497 (1963).
- 16) From the area of the main peak of Fig. 1, the yield of the TMS derivative of pentaerythritol was estimated to correspond to, at least, 7.8 mol% of the starting formaldehyde. The low yield is partly due to the loss during complex pretreatment of the reaction product to TMS derivative.

(Received September 21, 1984)