COS as an Electron Scavenger in Liquid-phase Radiolysis

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Although many compounds such as alkyl halides are known to dissociate after capturing an electron,[1] there are a few compounds which produce stable products after the dissociation.[2] Nitrous oxide is one such exceptional compound and has been extensively used in radiation chemistry.[3] The discovery of more such compounds is eagerly desired.

In the study of the γ-radiolysis of benzene, we have recently used COS as one of the solutes and have found that this compound produces CO as much as N_2 when nitrous oxide is used as a solute. Figure 1 shows the results obtained when the competition of COS and N_2O was examined. Obviously, the CO production from a COS-benzene solution decreased as the concentration of N_2O increased; the decrease in CO was about a half of the difference between the amounts of N_2 produced in the absence and in the presence of COS.*1 Since the G-value of N_2 from a N_2O-benzene solution is known to be approximately twice that of the electrons captured by N_2O,[4] the above observation can easily be explained by assuming the following reaction:

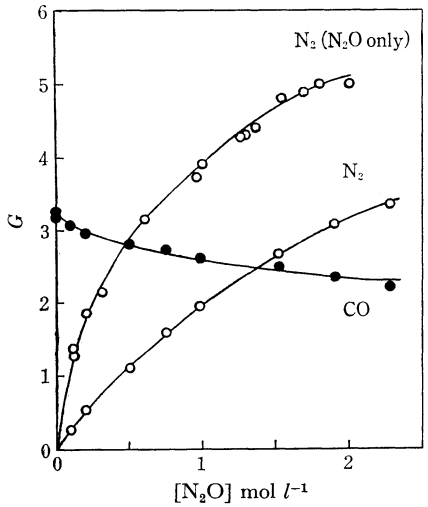

Fig. 1. The competition of COS and N_2O in the radiolysis of a benzene solution. The COS concentration is about 0.4 mol l^{-1}. (Direct decomposition of solutes is not corrected.)

$$e^- + COS \longrightarrow CO + S^-$$

or:

$$e^- + COS \longrightarrow COS^-$$

$$COS^- + C_6H_6^+ \longrightarrow CO + \text{residue}$$

At higher concentrations of N_2O, however, the amount of CO produced did not approach zero, but seemed to level off at a certain value. This is probably due to the reaction of COS with excited benzene molecules. If so, quantitative measurements will help the estimation of the ratio of ionization to excitation in the radiolysis of benzene.

We are now experimenting with COS as an electron scavenger in the radiolysis of saturated hydrocarbons. The results suggest that this compound is a little reactive to the radicals produced. This may cause some complications when analyzing the data. The details will be reported shortly.

1) J. M. Warman, K.-D. Asmus and R. H. Schuler, Advances in Chemistry Series, **82**, 25 (1968).

2) M. Matsui and M. Imamura, This Bulletin, **42**, 3362 (1969).

3) S. Sato, R. Yugeta, K. Shinsaka and T. Terao, *ibid.*, **39**, 156 (1966).

*1 Strictly speaking, this statement cannot be applied to the solutions with low N_2O concentrations.

4) R. R. Hentz and W. V. Sherman, *J. Phys. Chem.*, **73**, 2676 (1969).