BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3362—3363 (1969)

Acid Anhydride as an Electron Scavenger in the Radiolysis of Tetrahydrofuran

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(Received June 16, 1969)

Nitrous oxide has been used as a specific electron scavenger in radiation chemistry. In the cases of aqueous and neutral alcoholic solutions of nitrous oxide, the yield of nitrogen produced seems to reflect the yield of the solvated electron. On the other hand, more nitrogen is produced than is to be expected from the decrease in $G(H_2)$ in the radiolysis of hydrocarbon solutions[1-6] with lower dielectric constants.

This excess nitrogen formation may be interpreted by assuming, for example, the reaction of nitrous oxide with the O^- formed by the reaction between nitrous oxide and the solvated electron. An example of the electron-scavenging process including no such side reaction will be presented in this paper.

Experimental

Tetrahydrofuran (THF) (G.R., Junsei Chem. Co.) and methyltetrahydrofuran (MTHF) (R.G., K & K Lab., Inc.) were carefully dried on metallic potassium and distilled. Maleic anhydride (G.R., Kanto Chem. Co., Inc.) was recrystallized from ether or benzene solutions. Succinic, glutaric (G.R., Tokyo Kasei Ind. Co.) and phthalic anhydrides (G.R., Wako Pure Chem. Ind. Co.) were used as received. The gas fraction at $-196°C$ was determined on a conventional, calibrated gas burette and a Toepler pump. The hydrogen was determined by means of a heated palladium thimble, while the carbon monoxide and methane were analyzed gas-chromatographically by using a molecular sieve, 5A. Irradiation was carried out with a 10 kCi ^{60}Co source. The G-values were calculated on the basis of $G(Fe^{3+})=15.5$ and were corrected for the electron densities of THF and MTHF.

Results and Discussion

In the γ-radiolysis of liquid THF containing nitrous oxide, the amount of $G(N_2)$ always exceeds the decrease in $G(H_2)$.[7] The $G(H_2)$ decreases with an increase in the concentration of nitrous oxide, and $\Delta G(H_2)$ is seen to be 0.6 at the concentration of $(5-18)\times10^{-2}$M, where $G(H_2)$ is almost constant.

When the solutions of some aliphatic acid anhydrides in THF or MTHF were subjected to ^{60}Co-γ-irradiation at $20\pm1°C$ and at a dose rate of $(0.81—0.89)\times10^{17}$ eV$\cdot$m$l^{-1}\cdot$min^{-1}, it was found that $G(H_2)$ decreases with an increase in the concentration of acid anhydride, eventually reaching an approximately constant value which is practically the same as that observed for the THF-N_2O system. A typical example is illustrated in Fig. 1, where maleic anhydride is the solute.

Carbon monoxide is one of the gaseous products from THF, its yield is relatively low and is not affected by the addition of nitrous oxide and other solutes.[8] The $G(CO)$ in the THF-maleic anhydride

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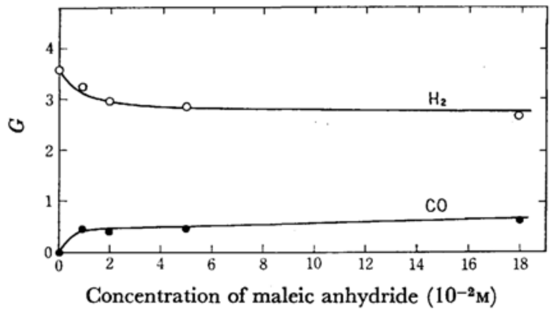

Fig. 1. Variation of $G(H_2)$ and $G(CO)$ with concentration of maleic anhydride.

system increases with an increase in the concentration of acid anhydrides. In Fig. 1, the difference between the total $G(CO)$ from the solution and that for pure THF, $G'(CO)$, is also plotted as a function of the concentration of maleic anhydride. It is interesting to note that the stationary value of $G'(CO)$ is approximately the same as that of $\Delta G(H_2)$. This fact presumably indicates that the precursor giving the additional carbon monoxide is that of hydrogen. It may be reasonable to assume that the solvated electron gives rise to the hydrogen formation in THF, as in MTHF[9] and alcoholic solutions,[10] *i. e.*, one solvated electron produces one hydrogen molecule. Therefore, it may be assumed that electrons react with the anhydrides to split off carbon monoxide, presumably by dissociative electron attachment.

Similar experiments have been carried out with a few other acid anhydrides. Succinic and glutaric anhydrides have been shown to behave much like maleic anhydride. Phthalic anhydride decreases the $G(H_2)$, but gives no additional carbon monoxide. The difference in reactivity is not clear at this moment.

The reactivities of these acid anhydrides towards electrons have been ascertained in experiments using the rigid matrix technique at 77°K. The optical absorption attributed to the matrix-trapped electron was found to diminish upon the addition of these additives.

An examination of the adaptability to other systems and of the mechanism of the carbon monoxide formation in the radiolysis of systems including acid anhydride is now in progress.

The authors wish to thank Dr. T. Shida for his rigid matrix work and Miss R. Maki for carrying out the gas-chromatographic analysis.

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