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The Radiolysis of a Binary Mixture of Tetrahydrofuran with Furan

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The radiolysis of a tetrahydrofuran(THF) and furan system was studied at a dose of about 2×10^{19} eV. ml^{-1} of ^{60}Co-γ-rays, and the hydrogen which may be formed by the no-ring opening and the carbon monoxide which should be formed by the ring scission were determined. The decrease in the hydrogen yield with an increase fraction of furan was found to be greater than had been expected, while G(CO) fit the expected value. The charge transfer mechanism was presumed for the decrease in the hydrogen yield in the γ-radiolysis of this mixture. Suggestions were made on the probable mechanism of the ring opening of the excited molecule for the formation of carbon monoxide, and on the ionic reaction for hydrogen formation. Furthermore, the probability of the ring scission of the THF molecule was roughly estimated by using the assumed decomposition reaction and the determined G values.

We have as yet very little information on the γ-radiolysis of liquid cyclic ethers, such as dioxane, tetrahydrofuran(THF) and furan. Granzow et al(1) have discussed the relevancy between the stability for ionizing radiation and the aromaticity of the compound by comparing the radiolysis of furan, thiophen and benzene. Llabador et al.(2) have determined the G values of the gas and liquid products in the γ-radiolysis of cyclic ethers and have discussed the reaction mechanism, especially that of the radiolysis of dioxane.

The present work was carried out in order to examine the existence of the protection in the radiolysis of the binary system of THF and furan system which has the lowest aromaticity among the heterocyclic compounds, and, furthermore, to establish the mechanism of the radiolysis of THF which is a typical heterocyclic compound.

Experimental

Materials. — The G. R.-grade furan was further purified by bulb-to-bulb distillation, the middle fraction was used for the run. The impurities in the furan were found to be negligible by gas chromatography. The G. R.-grade THF, stored with sodium hydroxide, was distilled through an about 50 cm., glass-helix-packed column at a reflux ratio of 10 : 1 after it had been refluxed with metallic potassium for about 24 hr.

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1) A. Granzow, J. Wedenburg and A. Henglein, *Z. Naturforsch.*, **19b**, 1015 (1964).

2) Y. Llabador and J. P. Adloff, *J. chim. phys.*, **61**, 681, 1467 (1964).

The fraction collected at 66.0—67.0°C was retained in storage vessel placed in the vaucum line in the dark. The remaining impurities were in the C_6 region and were found by gas chromatographic determination to total about 0.05%. These impurities were unchanged by γ-irradiation.

Sample Preparation, Irradiation and Analysis. —THF was distilled into a calibrated bulb from the storage vessel, and the middle fraction (about 10 ml.) was condensed into an irradiation cell. The furan for irradiation was prepared in a similar way.

These samples were subjected to ^{60}Co-γ-irradiation at 25.0 ± 1.0°C and at a dose rate of $(1.22—1.30) \times 10^{17}$ eV. ml^{-1} min^{-1}. The dose rate was determined by the Fricke method, assuming $G(\mathrm{Fe}^{3+}) = 15.6$, and $\varepsilon_{\mathrm{Fe}^{3+}} = 2150$ at 20.0°C and 304 mμ.

The gas fraction volatile at -196°C was determined on a conventional calibrated gas burette and a Toepler pump. The hydrogen content of the -196°C fraction was determined by means of a heated palladium thimble, while carbon monoxide was analyzed by the method using copper(II) oxide containing 1.3% iron(III) oxide, prepared by the method of Brücker and Schick.[3]

The fraction volatile at -80°C, consisting of C_2–C_4 hydrocarbons, and liquid products such as furan and butanol, was analyzed gas-chromatographically by using a 6 m. column of squalane at 30°C, and a 2.25 m. column of P. E. G.-1000 at 100°C.

Result and Discussion

If the radiolysis products of THF in a binary solution are unaffected by the presence of furan, the expected G value, G_{ex}, for a product, P, from the solution should be given approximately by the expression:

$$G_{ex}(\mathrm{P}) = G_{\mathrm{T}}{}^{0}(\mathrm{P})\varepsilon_{\mathrm{T}} + G_{\mathrm{F}}{}^{0}(\mathrm{P})\varepsilon_{\mathrm{F}}$$

where $G_{\mathrm{T}}{}^{0}(\mathrm{P})$ and $G_{\mathrm{F}}{}^{0}(\mathrm{P})$ refer to the yields of P from pure THF and furan respectively, and where ε_{T} and ε_{F} refer to the electron fraction in the solution radiolyzed. The G_{ex} values in Fig. 2 are represented by a linear dashed line.

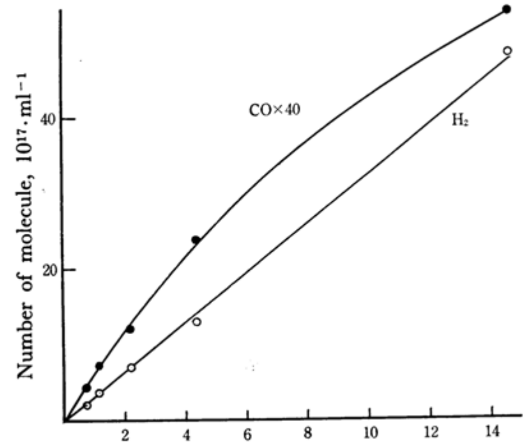

Fig. 1. The variation of $G(H_2)$ and $G(CO)$ with dose.

The hydrogen which may be formed by the no-ring opening, and the carbon monoxide which should be formed by the ring opening were determined in this binary system. Llabador and Adloff have shown that $G(H_2)$ and $G(CO)$ are independent of the total dose up to about 10^{20} eV. ml^{-1} in the radiolysis of liquid furan. Since a similar result was also obtained for THF in the region of low dosage, as is shown in Fig. 1, the binary system was irradiated at a dose of about 2×10^{19} eV. ml^{-1}.

The G value of the hydrogen and carbon monoxide from the purified liquid sample were 2.95 ± 0.22 and 0.13 ± 0.02 for THF, and 0.12 and 0.31 for furan. Those of the binary system of THF and furan are given in Table I and Fig. 2.

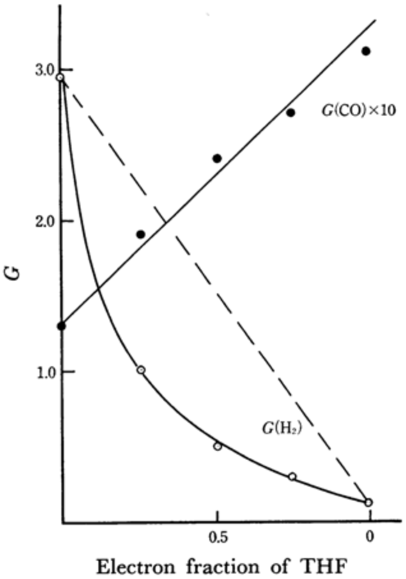

Fig. 2. Yields of H_2 and CO from the system THF-furan

TABLE I. YIELDS OF HYDROGEN AND CARBON MONOXIDE FROM MIXTURE OF THF AND FURAN IRRADIATED AT CA. 25.0°C AND 10^{19} eV. ml^{-1}

ε_{T}	$G(H_2)$ Obsvd.	$G(H_2)$ Calcd.	ΔG	$G(CO)$ Obsvd.	$G(CO)$ Calcd.	ΔG
1.00	2.95	2.95	0	0.13	0.13	0
0.74	1.01	2.21	−1.20	0.19	0.18	+0.01
0.49	0.50	1.51	−1.01	0.24	0.22	+0.02
0.25	0.29	0.83	−0.54	0.27	0.26	+0.01
0	0.12	0.12	0	0.31	0.31	0

The decrease in the hydrogen yield is shown to be greater than that to be expected from the above equation, whereas the yields of carbon monoxide fit the expected values. According to the current

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[3] H. Brückner and R. Schick, *Gas u. Wasserfach.*, **82**, 189 (1939).

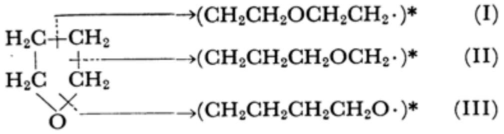
theories of radiation chemistry, radiolysis begins with the production of molecules of vibrationally- and electronically-excited state, in addition to that of ionic species. The different mechanisms may be possible for the formation of hydrogen and carbon monoxide in the radiolysis of liquid THF.

The decrease in hydrogen yield might be due to the protection of THF from reaction by an activation transfer mechanism which reduces the amount of the initial decomposition of the THF itself; it might be due to a scavenging process that removes precursors of hydrogen, or it might be due to a combination of the two.

The yields of hydrogen and carbon monoxide from neither THF nor furan are affected by adding I_2 and hydroquinone respectively as radical scavengers. Their constant G values were also observed by adding ethylene (0.56—3.55 mol.) in the γ-radiolysis of THF. Moreover, if furan acts as the scavenger for the H-atom, the amount of residual hydrogen should be constant at a high concentration of added furan. However, this is not the case, as is shown in Fig. 2. Consequently, there should be no hydrogen atoms scavenged by the added furan, and the decrease in $G(H_2)$ in the radiolysis of the THF-furan system might be due to the "sponge-type" protection[4] action of furan with relation to THF.

Since $G(CO)$ and the amount of constructional units containing oxygen atoms in the THF molecule are both half of those of dioxane, the mechanism of the formation of the carbon monoxide in the γ-radiolysis of THF may be similar to that of dioxane. Llabador and Adloff have suggested that the decomposition of the excited dioxane molecule gives rise to the formation of carbon monoxide. Furthermore, in the photolysis of ethyleneoxide, the ring opening was the main reaction, and in the mercury-sensitized photolysis of de-aerated THF, the ratio of carbon monoxide to hydrogen was about 10 times that in the γ-radiolysis. Therefore, it may be concluded that the excited molecule of THF is the most important precursor of the formation of carbon monoxide, though its energy state is not yet clear. However, the excitation transfer which is related to the reaction can not be assumed in this binary system, since $G(CO)$ fits the expected values, as has been seen in Fig. 2.

The mode of the ring opening in the THF molecule is supposed to be as follows:



$\rightarrow (CH_2CH_2OCH_2CH_2\cdot)^*$ (I)

$\rightarrow (CH_2CH_2CH_2OCH_2\cdot)^*$ (II)

$\rightarrow (CH_2CH_2CH_2CH_2O\cdot)^*$ (III)

The carbon monoxide should be formed by the decomposition of the active species, such as I, II and III, when those species have excess energy after the ring opening. If the C–O bond rupture also occurs preferentially in these active species, as has been suggested by Newton[5] and, Ng and Freeman[6] in the α-and γ-radiolysis of linear ethers respectively, the formation of carbon monoxide may be explained by the following scheme:

$$\text{I} \longrightarrow (CH_2CH_2\cdot)^* + (OCH_2CH_2\cdot)^* \quad (1)$$

$$(CH_2CH_2\cdot)^* \longrightarrow C_2H_4 \text{ or } C_2H_5\cdot \quad (2)$$

$$(OCH_2CH_2\cdot)^* \xrightarrow{C_4H_7O\cdot} CO + CH_3\cdot + C_4H_8O \quad (3)$$

$$CH_3\cdot + C_4H_8O \longrightarrow CH_4 + C_4H_7O\cdot \quad (4)$$

According to Llabador's data, since the yields of ethylene and carbon monoxide indicate the "molecular" yield and since 90% methane was scavenged by the radical scavenger, the reactions 1, 2 and 3 may be taking place in the spur region. Carbon monoxide is considered to be formed also by the following scheme:

$$\text{II} \longrightarrow (CH_2CH_2CH_2\cdot)^* + (OCH_2\cdot)^* \quad (5)$$

$$(OCH_2\cdot)^* \longrightarrow CO + H_2 \quad (6)$$

$$(CH_2CH_2CH_2\cdot)^* \longrightarrow CH_3\text{-}CH{=}CH_2 \text{ or } (CH_2)_3 \text{ or } C_3H_7\cdot \quad (7)$$

As the yields of propylene, cyclopropane, CO and H_2 indicate the "molecular" yield in Llabador's data at a high dosage, while no cyclopropane and only a trace of propylene were determined in the low-dosage experiment of this report, reactions 5, 6 and 7 may occur in spur region anyhow. A similar process may be presumed for the III species as follows:

$$\text{III} \longrightarrow CH_3CH_2CH_2CH_2OH \quad (8)$$

$$\text{III} \xrightarrow{C_4H_7O\cdot} CO + C_3H_7\cdot + C_4H_8O \quad (9)$$

$$C_3H_7\cdot + C_4H_8O \longrightarrow C_3H_8 + C_4H_7O\cdot \quad (10)$$

The decrease in $G(C_3H_8)$ caused by the added radical scavenger in Llabador's data at high dosage may be explained qualitatively by assuming the reactions 7 and 9 in the spur. Since $G(C_3H_8)$ is negligible in the low-dosage experiments of this report, reaction 8 may be more dominant than 9.

The probability of the formation of active species I, II and III by ring opening can roughly be estimated as I : II : III$=1.0 : \sim 0 : 1.3$, by using the above scheme, and the results determined at a total does of 4.39×10^{19} eV. ml^{-1}. These results are $G(C_4H_9OH)=0.40$, $G(CH_4)=0.01$, $G(C_2H_4)=0.30$, $G(C_2H_6)=0$, $G(c\text{-}C_3H_6)=0$, $G(C_3H_6)=$trace and $G(C_3H_8)=$trace. It may be presumed, by taking its estimated value, that the probability of the C–O bond rupture is a little greater than

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[4] M. Burton and S. Lipsky, *J. Phys. Chem.*, **61**, 1461 (1957).

[5] A. S. Newton, *J. Phys. Chem.*, **61**, 1485, 1490 (1957).

[6] M. K. M. Ng and G. R. Freeman, *J. Am. Chem. Soc.*, **87**, 1635, 1639 (1965).

the rupture of the C(β)–C(β') bond. The actual ratio of ring opening might be greater than these estimated values, depending upon the identity of the dimeric and polymeric products.

As for the formation of the hydrogen in this binary system, a charge transfer is probable. A positive ion of THF may easily be formed by ejecting, by means of ionizing radiation, one of the lone-pair electrons located at the oxygen atom. Since the ionization potentials of THF and furan are 10.3 and 9.06 eV. respectively, the charge transfer from the ground state of the THF ion to a furan molecule is probable, because the process is exothermic. Therefore, an ionic reaction, such as an ion-molecule reaction or an ion recombination reaction, is most probable for the formation of the hydrogen.

Dainton et al.[7] have suggested that the dominant primary species formed in the γ-radiolysis of methyltetrahydrofuran (MTHF) in the glassy state are an electron and a free radical (corresponding to the solvent molecule minus a hydrogen atom), followed by the ion-molecule reaction between MTHF and its ion. The experimental finding that the hydrogen yield was unaffected by an added radical scavenger could also be explained by the process of the ion-molecule reaction, because the "molecular" hydrogen is produced by this reaction. As the formation of "molecular" hydrogen may also be considered in the ion-recombination reaction, which is another process of the parent ion, it is convenient to conclude that the hydrogen is formed mainly by the ionic reaction, and that the precursor of the carbon monoxide is the directly-excited THF molecule.

Summary

The charge transfer is presumed for the formation of hydrogen in the γ-radiolysis of liquid THF-furan mixtures. The ring opening of the excited molecule has been suggested to be the main process in the formation of carbon monoxide. It has also been suggested that hydrogen might be formed mainly by an ionic reaction including the parent positive ion of THF. The probability of the ring opening has been roughly estimated.

The author's thanks are due to Dr. Kenichi Shinohara, Masashi Imamura and Ko Taki for their stimulating discussions of the problems, and to Miss Noriko Tsunoo for her analysis by gas chromatography.

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[7] F. S. Dainton, J. P. Keene, T. J. Kemp, G. A. Salmon and J. Teply, *Proc. Chem. Soc.*, **1964**, 265; F. S. Dainton, F. R. S., and G. A. Salmon, *Proc. Roy. Soc.*, **A285**, 319 (1965).