[August, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (8), 2191—2194 (1978) 2191

The Radiolysis of Binary Mixtures of Tetrahydrofuran with Benzene, Thiophene, Pyridine, and Nitrobenzene

Masao MATSUI* and Masashi IMAMURA†

Department of Pharmacy, Hokuriku University, Kanagawa-machi, Kanazawa-shi, Ishikawa 920-11

†*The Institute of Physical and Chemical Research, Wako-shi, Saitama 351*

(Received January 17, 1978)

Binary mixtures of tetrahydrofuran (THF) with benzene, thiophene, and nitrobenzene were subjected to radiolysis with γ-rays. The THF–benzene mixture was also irradiated with 28.6 MeV ^{4}He- and 90.9 MeV ^{12}C-ions. For THF–benzene mixtures, similar deviations of $G(H_2)$ from the mixture law were observed for all the radiolyses; these results are regarded as being due to energy transfer from THF^{+}, the precursor of hydrogen, to benzene. The total ionization yield of THF was calculated as 3.0—3.3 in G-units, irrespective of radiation and additives. This is on the basis of Hardwick's procedure, in which the deviations of $G(H_2)$ are divided by the efficiency of the energy transfer. This result also indicates that the total ionization yield is independent of the nature of radiation, whose LET range is from 0.02 to 49.2 eV/Å.

In the radiolysis of binary mixtures of organic liquids, a deviation from the mixture law$^{1)}$ is sometimes observed. This deviation has been interpreted as a result of an energy or charge transfer from one component to the other.

Hardwick$^{2)}$ has shown that the efficiency of an energy or charge transfer can be estimated from these deviations. When a radiolysis product is formed from an ionic precursor which can transfer its charge to the other component of the binary mixture, one can calculate a total ionization yield by combining the limiting efficiency of the charge transfer with the deviation of the product yield from the expected one.

One of the present authors$^{3)}$ has previously reported that the hydrogen yield from a binary mixture of tetrahydrofuran (THF) and furan shows a deviation from the mixture law in the γ radiolysis and that the decrease in $G(H_2)$ is due to the charge transfer from THF to furan.

In the present study, binary mixtures of THF with benzene, thiophene, pyridine, and nitrobenzene as well as furan were subjected to irradiation with γ rays; the THF–benzene mixture was also irradiated with He- and C-ions. Moreover, the total ionization yields of THF, calculated by Hardwick's procedure, were compared with that of γ radiolysis.

Experimental

Materials. The THF was purified as has been described in a previous paper.$^{4)}$ The thiophene (Tokyo Kasei Guaranteed Reagent) and benzene (Junsei Pure Chem. Guaranteed Reagent) were purified gas-chromatographically using a 3-m column of PEG-1000 at 100 °C. The pyridine (Wako Pure Chem. Extra Pure Reagent) and nitrobenzene (Wako Pure Chem. Guaranteed Reagent) were kept on sodium hydroxide and calcium chloride respectively for several days before rectifying.

Irradiation. γ-irradiation was carried out with a 10-kCi ^{60}Co source at a dose rate of 5.85×10^{17} eV g^{-1}min^{-1} (9370 rad min^{-1}), which was determined by using a Fricke dosimeter on the basis of $G(Fe^{3+})=15.6$. The G-values were calculated after the correction of the absorbed dose for the electron densities of the solutions used. The He-(28.6 MeV) and C-(90.9 MeV) ions were accelerated with the cyclotron at the Institute of Physical and Chemical Research. The current intensity and total dose for charged particles were $\approx$1 nA and (3.6—5.0) $\times 10^{19}$ eV respectively. The samples were vigorously stirred with a magnetic stirrer during irradiation at an ambient temperature.

The details of the irradiation arrangement and experimental procedures for charged-particle radiolysis were the same as those described previously.$^{5)}$

Analysis of Products. The gaseous fraction at −196 °C was determined on a conventional calibrated gas burette and a Toepler pump. The hydrogen and carbon monoxide were determined by gas chromatography using a Molecular Sieve 5A.

Results and Discussion

γ Radiolysis of THF–Benzene and THF–Thiophene Mixtures. The yield of hydrogen from pure liquid THF was $G=3.5$ in the present study, in agreement with several values previously reported.$^{4,6)}$ The hydrogen yields for the binary mixtures of THF–benzene and THF–thiophen are plotted as a function of the electron fractions of benzene and thiophene respectively in Figs. 1 and 2. In both cases, the yields are lower than those to be expected from the mixture law. A similar trend of $G(H_2)$ has been observed for the THF–furan mixture,$^{3)}$ whose concave variation of $G(H_2)$ was interpreted as being due to charge transfer from THF cations to furan molecules. For the THF–benzene and THF–thiophene mixtures, the deviation from straight

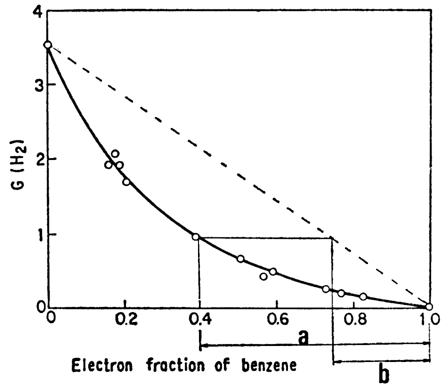

Fig. 1. Hydrogen yields from THF–benzene mixtures in γ radiolysis.

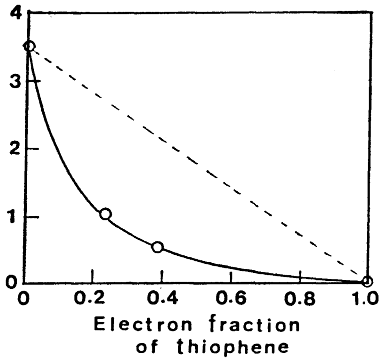

Fig. 2. Hydrogen yields from THF–thiophene mixtures in γ radiolysis.

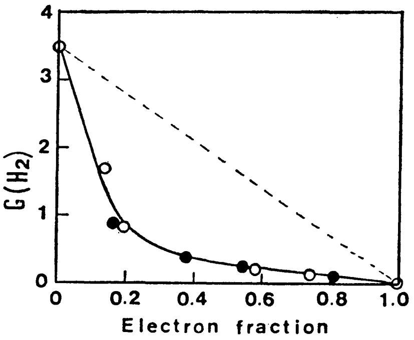

Fig. 3. Hydrogen yields from THF–pyridine (○) and THF–nitrobenzene (●) mixtures in γ radiolysis.

lines connecting the $G(H_2)$'s of THF and additives may also be explained on the same basis. In the γ radiolysis of THF, hydrogen was found to be produced molecularly; *i.e.*, the $G(H_2)$ was not affected by adding radical scavengers.[3] Most of the hydrogen is considered to be formed by rapid ion-molecule reactions of THF^+.[7] Therefore, the deviation of $G(H_2)$ from the mixture law may reasonably be explained in terms of charge transfer from THF^+ to the additives whose hydrogen yields are lower than that of THF.

This argument is supported by the facts that the ionization potentials[8] of benzene, thiophene, and furan are lower (9.25, 8.86, and 8.89 eV respectively) than that of THF (9.54 eV) and that the maximum deviations of $G(H_2)$, which appear at an electron fraction of about 0.25 for the above three additives, are in the order of the ionization potentials of the additives.

A similar relation has been observed in the production of D_2 and HD for the liquid-phase radiolysis of several binary mixtures of ethane-d_6, propane-d_8, and butane-d_{10} in liquid hydrocarbons at 195 K. That is, solvents with higher ionization potentials enhance the production of D_2 and HD from deuterated solutes with lower ionization potentials. There is also a great deal of evidence indicating that charge transfer to, or the positive-ion scavenging of, benzene takes place in liquid and glassy solutions.[10–18]

The occurrence of the charge transfer from THF^+ to benzene is further supported by the fact that the $\Delta G(H_2)$ of the THF–benzene mixture was reduced on the addition of triethylamine, that is, a positive-ion scavenger. For example, $\Delta G(H_2)=1.10$ in the THF–benzene ($a=0.2$) mixture was reduced to 0.55 on the addition of both benzene ($a=0.12$) and triethylamine ($a=0.08$) to THF. Since the $G(H_2)$ from pure triethylamine is higher than that of THF, the $G(H_2)$ for the THF–triethylamine mixture is increased by transferring the charge from THF^+ to triethylamine.

In contrast to $G(H_2)$, $G(CO)$ varies linearly with the electron fraction of the additives. Carbon monoxide has been shown to be produced from excited THF,[3] therefore, its yield is expected not to be affected by the presence of charge scavengers.

γ Radiolysis of THF–Pyridine and THF–Nitrobenzene Mixtures. Concave variations in $G(H_2)$ apparently similar to those observed for the THF–benzene and THF–thiophene mixtures described in the previous section were also observed for THF–pyridine and THF–nitrobenzene mixtures. It should be noted, however, that no substantial difference was observed between the two mixtures, as is shown in Fig. 3.

Either of these two additives has not only an ionization potential higher than that of THF, but also a high rate-constant toward hydrated electrons: $k(\text{pyridine}+e^-_{aq})=3.7\times10^9\ M^{-1}\,s^{-1}$ and $k(\text{nitrobenzene}+e^-_{aq})=3.0\times10^{10}\ M^{-1}\,s^{-1}$,[19] which are 10^2—10^3 times those of benzene ($k=1.4\times10^7\ M^{-1}\,s^{-1}$), thiophene ($k=3.0\times10^6\ M^{-1}\,s^{-1}$), and furan ($k=6.5\times10^7\ M^{-1}\,s^{-1}$).[19]

These facts indicate that, in the THF–pyridine and THF–nitrobenzene mixtures, the additives could act as efficient electron scavengers to reduce $G(H_2)$ from THF. Hydrogen is produced from THF by the reaction of electrons with the $THFH^+$ produced by the ion-molecule reaction (THF^++THF) as well as by the decomposition of excited THF molecules within spurs. Therefore, insofar as additives react with solvated electrons at a diffusion-controlled rate, the variation in $G(H_2)$ with the electron fraction should be independent of the nature of the additive. In fact, the $G(H_2)$-values from THF–pyridine solutions containing carbon tetrachloride were found to fit the curve in Fig. 3 when plotted *vs.* the sum of the electron fractions of pyridine and carbon tetrachloride.

He- and C-ion Radiolysis of THF–Benzene Mixture. The radiolysis of the THF–benzene mixture was carried out with 28.6 MeV He- and 90.9 MeV C-ions. The results are shown in Fig. 4, where the observed $G(H_2)$'s are plotted as a function of the electron fraction of benzene. Although the hydrogen yields from both THF and benzene are higher than those in the γ radiolysis, the variations in the $G(H_2)$ are qualitatively similar to those in the γ radiolysis. Thus, the charge transfer from THF^+ to benzene can be assumed to explain the concave variation in $G(H_2)$ in the He- and C-ion radiolysis.

Total Ionization Yields and Their LET-Dependence. Assuming that the additives act as charge acceptors (benzene, thiophene, and furan) or electron acceptors (pyridine and nitrobenzene) in the THF solutions, and that hydrogen is produced only from THF^+ and excited THF, one can calculate the total ionization yields in γ and heavy-ion radiolyses by using the procedure proposed by Hardwick.[2]

When a stands for the electron fraction of THF in the

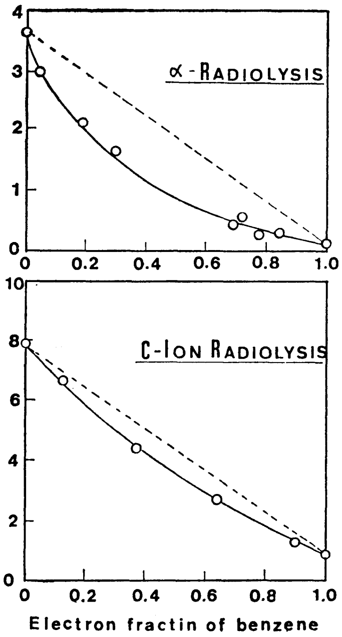

Fig. 4. Hydrogen yields from THF–benzene mixtures in He- and C-ion radiolysis.

mixture, and *b*, the apparent fraction of THF, as indicated by the measured value of $G(H_2)$ (see Fig. 2), the amount of THF which transfers energy is given by $(1-b)-(1-a)=a-b$. The fraction of THF molecules transferring a charge to acceptor molecules is, therefore, $(a-b)/a$.

The limiting values of $(a-b)/a$ can be obtained by plotting $(a-b)/a$ as a function of the electron fractions of the additives. In the γ radiolysis, such plots gave the limiting values of 0.70—0.75, identical within the range of experimental error for the THF–benzene, THF–thiophene, and THF–furan mixtures; these results are in accord with those obtained for alkane mixtures.$^{2)}$ As Hardwick has stated, the identical limiting values for these mixtures may indicate that the characteristics of the donor molecule rather than those of the acceptor molecule govern the transfer process.

The limiting values of $(a-b)/a$ obtained with THF–benzene mixtures for He- and C-ion radiolysis were 0.65 and 0.50 respectively. Since THF in the THF–benzene, THF–thiophene, and THF–furan mixtures has an ionization potential lower than those of the additives, the energy transfer taking place in these systems may be regarded as a charge transfer. This assumption may also support the above findings as to the very close limiting values of $(a-b)/a$ for these mixtures. The remaining molecules, which do not transfer but decompose to give products, may, as Hardwick argued, be considered to be electronically excited. As has been mentioned above, in the He- and C-ion radiolyses the limiting values of $(a-b)/a$ were found to be 0.65 and 0.50 respectively for the THF–benzene mixtures. These values are lower than that obtained in γ radiolysis and show a substantial LET dependence. This fact, on the assumption mentioned above, indicates that the relative yield of electronically excited states which decompose to give products is substantially increased in high LET radiolyses.

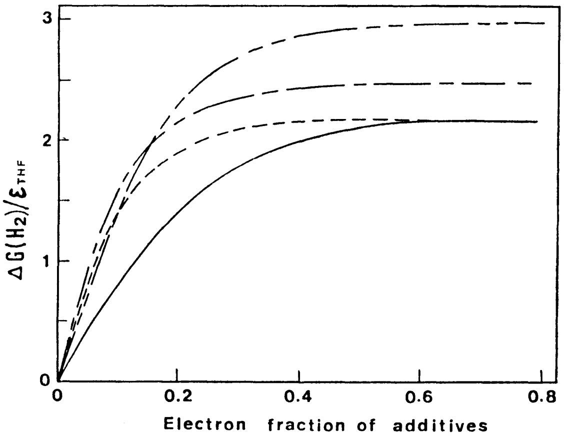

Fig. 5. Effectiveness of additives in γ radiolysis. Benzene (——), thiophene (– – –), furan (– – –), pyridine and nitrobenzene (– – –).

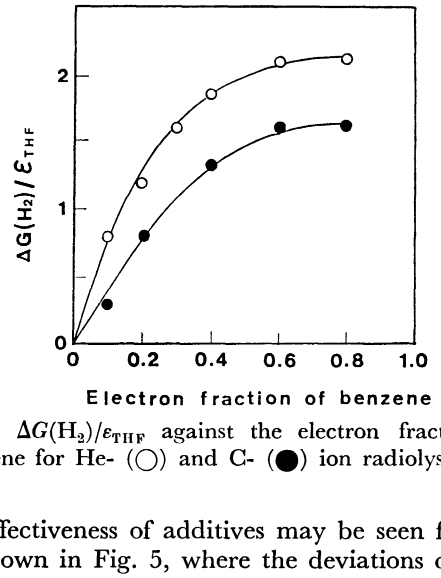

Fig. 6. $\Delta G(H_2)/\varepsilon_{THF}$ against the electron fraction of benzene for He- (○) and C- (●) ion radiolysis.

The effectiveness of additives may be seen from the curves shown in Fig. 5, where the deviations of $G(H_2)$ from the mixture law divided by the electron fraction of THF are plotted against the electron fraction of additives. For the He- and C-ion radiolyses, the deviations from the mixture law divided by the electron fraction of THF, $\Delta G(H_2)/\varepsilon_{THF}$, are shown in Fig. 6 as a function of the electron fraction of benzene. From Figs. 5 and 6 it is apparent that the limiting values of $\Delta G(H_2)$ corresponding to the limiting fraction of the THF-transferring charge are 2.2—2.5 for γ radiolysis and 2.1 and 1.6 for He- and C-ion radiolyses respectively.

On the other hand, a limiting $\Delta G(H_2)$-value of 2.9 is obtained by a similar treatment of the results observed for the γ radiolysis of THF–pyridine and THF–nitrobenzene mixtures in Fig. 5. Since these additives are thought to act as electron scavengers to reduce $G(H_2)$ from THF, and since the limiting value of $\Delta G(H_2)$ obtained is much the same as that of $G(e^-)$ reported by Baxendale *et al.*,$^{20)}$ this value may represent the yield of electrons. They have determined the G(ion pair) values of 2.6 and 2.7 for the pulse radiolysis of THF–pyrene (5 mM)–$LiAlH_4$ (maximum$\simeq$0.45 M) and the γ radiolysis of THF–carbon tetrachloride (maximum$\simeq$ 0.1 M) mixtures respectively.

Shaede *et al.*[21] have also observed a total ionization yield of 3.75 for the nanosecond pulse radiolysis of a THF–pyrene mixture. The difference between $G(\mathrm{THF}^+)$ and $G(\mathrm{e}^-)$ estimated by the above-described treatment is probably attributable to the discrepancy of the efficiency between electron transfer and electron capture.

If one can assume that benzene acts solely as a charge acceptor in the present binary mixtures, the "total ionization yield" may be obtained by dividing the limiting value of $\Delta G(\mathrm{H}_2)$ by that of $(a-b)/a$. The value of 3.0—3.1 is obtained for the γ radiolysis systems and that of 3.2—3.3 for the heavy-ion radiolysis systems. No substantial difference in the total ionization yield is seen between the two systems. These results reflect the fact that the ionization yield of liquid THF is independent of LET over a wide range and that the increased yields of hydrogen observed for heavy-ion-radiolysis systems may be attributable to the increased yields of the excited states.

The author's thanks are due to Messrs. Kazuo Otsuka and Yasuo Harata, who helped us throughout this work.

References

1) The mixture law states that energy is initially absorbed in a mixture in proportion to the electron fraction's relationship to the components. *Cf.* J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952); R. A. Holroyd, in "Fundamental Processes in Radiation Chemistry," ed by P. Ausloos, Interscience, New York (1968), Chap. 7, p. 493.

2) T. J. Hardwick, *J. Phys. Chem.*, **66**, 2132 (1962).

3) M. Matsui, *Bull. Chem. Soc. Jpn.*, **39**, 1640 (1966).

4) M. Matsui and M. Immamura, *Bull. Chem. Soc. Jpn.*, **42**, 3362 (1969).

5) M. Matsui and M. Imamura, *Bull. Chem. Soc. Jpn.*, **47**, 1113 (1974).

6) F. S. Dainton and G. A. Salmon, *Proc. R. Soc. London, Ser. A*, **285**, 319 (1965).

7) J. H. Baxendale, D. Beaumond, and M. A. J. Rodgers, *Int. J. Radiat. Phys. Chem.*, **2**, 39 (1970).

8) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).

9) J. A. Stone, A. R. Quirt, and O. A. Miller, *Can. J. Chem.*, **44**, 1175 (1966).

10) L. I. Bone and J. H. Futrell, *J. Chem. Phys.*, **47**, 4366 (1967).

11) L. Y. Wei and L. I. Bone, *J. Phys. Chem.*, **75**, 2272 (1971).

12) K. N. Jha and G. R. Freeman, *Can. J. Chem.*, **49**, 2651 (1971).

13) M. G. Kennedy and J. A. Stone, *Can. J. Chem.*, **51**, 149 (1973).

14) J. K. Thomas and I. Mani, *J. Chem. Phys.*, **51**. 1834 (1969).

15) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2375, 4372 (1966).

16) A. Ekstrom, *J. Phys. Chem.*, **74**, 1705 (1970).

17) F. W. F. Louwrier and W. H. Hamill, *J. Phys. Chem.*, **74**, 1418 (1970).

18) P. S. Rudolph and C. E. Melton, *J. Chem. Phys.*, **32**, 586 (1960).

19) M. Anbar, M. Bambenek, and A. B. Ross, "Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution. 1. Hydrated Electron," NSRDS-NBS 43, Washington, D. C. (1973).

20) J. H. Baxendale, D. Beaumond, and H. A. J. Rodgers, *Trans. Faraday Soc.*, **66**, 1966 (1970).

21) E. A. Shaede, H. Kurihara, and L. M. Dorfman, *Int. J. Radiat. Phys. Chem.*, **6**, 47 (1974).