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Effect of Nitrous Oxide on the Radiolysis of Liquid Methanol with the Recoils from the ^{10}B(n, α)^{7}Li Reaction

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Liquid methanol containing trimethyl borate and nitrous oxide was irradiated with thermal neutrons from a nuclear reactor. In contrast to the marked effect on the γ-radiolysis yields, nitrous oxide had a little effect on the recoil radiolysis yields from methanol, and nitrogen yield was as low as 0.2 in G unit. These results indicate that the yield of the solvated electron in the recoil radiolysis of methanol is about one tenth of that in the γ-radiolysis.

A number of studies have been carried out on the hydrated electrons in aqueous solutions by means of the pulse radiolysis technique and chemical kinetics.[1,2] The formation of solvated electrons in aliphatic alcohols has also been demonstrated by similar techniques.[2] In liquid methanol, G values (100 eV-yield) of the solvated electron produced by γ-irradiation have been determined,[2-4] all of which are substantially lower than the value, $G=2.0$, obtained by the present authors using the nitrous oxide scavenging method.[5,6]

Apart from γ-radiolysis, no experiment has been reported on the yield of solvated electrons, to authors' knowledge, except one by Henglein, Asmus, Scholes and Simic on the aqueous nitrous oxide solutions irradiated with the recoils from the ^{10}B(n, α)^{7}Li reaction.[7] Their $G(N_2)$ is much lower than that for the γ-radiolysis, indicating a very low yield of the hydrated electron in the radiolysis with such a high LET (linear energy transfer) radiation. Very low yields of solvated electrons were reported also for the recoil radiolysis of ethanol and methyltetrahydrofuran glasses at −196°C,[8] in contrast to the high yields for the γ-radiolysis.[9]

In the radiolyses with high LET radiations, higher molecular yields and lower radical yields are expected. It is generally accepted that such LET effects result from the increase in the recombination of free radicals inside spurs with increasing LET and from other effects associated with high LET radiations. Therefore, the decrease in the yield of (scavengable) solvated electrons with increasing LET of radiation may also be expected. This paper reports the effects of nitrous oxide used as an electron scavenger in the liquid methanol irradiated with the high LET recoils from the ^{10}B(n, α)^{7}Li reaction.

Experimental

Materials. Eastman Spectrograde methanol was fractionated after refluxing with sodium borohydride for about 6 hr. The middle third of the distillate was taken and dried over $Mg(OCH_3)_2$ prepared by dissolving magnesium turnings.[10]

Trimethyl borate obtained from Callery Chemical Co. was further purified by distillation in the dry nitrogen atmosphere and stored in a degassed ampoule.

Pure nitrous oxide (>99.9%) was obtained from Takachiho Chemical Co. and was re-distilled in vacuo at liquid nitrogen temperature.

Irradiation Ampoules. Irradiation ampoules were made of quartz. The ampoule (2 cm diameter and 10 cm high) was equipped with a quartz breakseal for gas analysis and a quartz ground joint for preparing sample. These ampoules were cleaned carefully by using acid dichromate solution and finally rinsed thoroughly with triply-distilled water.

Sample Preparation. The irradiation ampoule was degassed thoroughly for several hours by baking and Tesla-discharging. Dry methanol was introduced into the ampoule by vacuum-distillation after being degassed by repeated chill-pump-thaw cycles and distillation. A dennite amount of trimethyl borate was taken in a small weighing ampoule by distillation and then added to methanol in the ampoule. The amount of borate added was determined by weighing; the con-

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[1] See for example "Solvated Electron," Advances in Chemistry Ser. 50, R. F. Gould, Ed., Am. Chem. Soc., Washington D. C. (1965).

[2] L. M. Dorfman and M. S. Matheson, "Progress in Reaction Kinetics," Vol. 3, G. Porter Ed., Pergamon, Oxford (1965), p. 237.

[3] J. H. Baxendale and F. W. Mellows, *J. Am. Chem. Soc.*, **83**, 4720 (1961).

[4] E. Hayon and M. Moreau, *J. Phys. Chem.*, **69**, 4053 (1965).

[5] H. Seki and M. Imamura, This Bulletin, **38**, 1229 (1965).

[6] H. Seki and M. Imamura, *J. Phys. Chem.*, **71**, 870 (1967).

[7] A. Henglein, K.-D. Asmus, G. Scholes and M. Simic, *Z. phys. Chem. N. F.*, **45**, 39 (1965).

[8] J. Wendenburg and A. Henglein, *Z. Naturforsch.*, **19b**, 995 (1964).

[9] J. P. Guarino, M. R. Ronayne and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962).

[10] For further details, see M. Imamura, S. U. Choi and N. N. Lichtin, *J. Am. Chem. Soc.*, **85**, 3565 (1963).

centration of borate was in the range of 0.24—0.30 M. A definite amount of nitrous oxide was added to the solution frozen in the ampoule at liquid nitrogen temperature. The ampoule was then sealed off under pumping at liquid nitrogen temperature. The concentration of nitrous oxide was calculated from the solubility data in pure methanol.[11]

Irradiation. The thermal neutron irradiation facility of the nuclear reactor at the Atomic Research Laboratory of Musashi Institute of Technology, Kawasaki, was used.[12] The thermal neutron flux was in the order of 10^9 cm^{-2} sec^{-1} and the epithermal neutron flux was estimated to be in the order of 10^8 cm^{-2} sec^{-1}. The chemical effect of the background γ-rays was determined as mentioned below and was found to be negligible under the present experimental conditions.

Dosimetry. The thermal neutron flux and the dose rate of the 2.35 MeV α,^{7}Li-recoils were determined with the Fricke dosimeter containing 0.022 M boric acid on the basis of $G(Fe^{3+})=4.22$.[13] The thermal neutron flux for each ampoule was monitored with a gold foil attached to each ampoule. The thermal neutron fluxes obtained from gold foils[14] attached to dosimeter ampoules were always higher than those from corresponding chemical dosimeters.[15] Data obtained from the chemical method were tentatively taken as standard thermal neutron fluxes, and the flux for each ampoule containing methanol was corrected by using the relative value obtained with gold foils attached to the sample ampoule and the dosimeter ampoule. Total dose of the recoil energy was between 1.6×10^{19} and 3.0×10^{19} eV/m*l* (complete absorption assumed).

The dose rate of the background γ-rays was determined with the normal Fricke dosimeter on the basis of $G(Fe^{3+})=15.6$. γ-Ray energy absorbed by the solution was found to be less than 5% of the recoil energy. The results of chemical dosimeter for recoils were subjected to the correction for the background γ-rays; the yields of products were practically not affected by the correction within the limits of experimental errors.

Analyses. Analytical methods and procedure employed in this study were essentially similar to those described elsewhere.[16] Product gas was carefully removed by Toepler-pumping from the irradiated solution at dry ice temperature through a liquid nitrogen trap, in which unreacted nitrous oxide as well as methanol vapor was eliminated. Collected gas was then subjected to analysis by microcombustion method and the remaining gas was assumed to be nitrogen.[17]

Formaldehyde and ethylene glycol were determined by chromotropic acid method.[16] It has been found that trimethyl borate or boric acid interferes the color development in the analysis of formaldehyde.[16] One milliliter of 25% aqueous chromotropate solution was used instead of 0.5 m*l* of 10% solution for 1.0 m*l* sample solution.[18]

Results and Discussion

Radiolysis yields obtained in the presence and absence of nitrous oxide are summarized in Table 1. Recoil radiolysis yields for "pure" methanol[19] have been reported by Lichtin and his coworkers.[10,20,21] From these results it may reasonably be accepted that $G(H_2)$ ~5.5, $G(CO)$ ~1.0, $G(CH_4)$ ~0.5—0.7, $G(CH_2O)$ ~3.0—3.5 and $G(C_2H_6O_2)$ —0.6—0.9. Although the results listed in Table 1 are considerably scattered, the yields for "pure" methanol could be compared with above ones.

In the γ-radiolysis of liquid methanol, $G(H_2)$ decreases to 3.3 and $G(N_2)$ reaches 2.1 at the nitrous oxide concentration of 5×10^{-3} M.[5] Above this concentration, $G(H_2)$ and $G(N_2)$ show very slow decrease and increase, respectively. Extension of the curves in the high concentration range to zero nitrous oxide concentration gives 3.4 and 2.0 for $G(H_2)$ and $G(N_2)$, respectively.[6] The yields of formaldehyde and ethylene glycol also vary but not so rapidly as those of H_2 and N_2 in the low concentration range; both $G(CO)$ and $G(CH_4)$ remain unchanged. From these results together with the competition kinetics of hydrogen ions, it has been concluded that nitrous oxide scavenges only electrons that may be solvated and lead to the formation of products in the absence of nitrous oxide.[5,6]

In the present recoil radiolysis study, on the other hand, no such a marked effect of nitrous oxide can be observed. Nitrogen is produced with $G=0.2$ (except for run No. 6 which may be erroneous) over the entire concentration range of nitrous oxide studied; the decreasing yield of hydrogen cannot be concluded quantitatively under the present experimental conditions.

However, also in the recoil radiolysis, nitrous oxide may be expected to scavenge only solvated electrons that escape cylindrical tracks and lead to the formation of products in the absence of

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[11] Intern. Critical Tables, **3**, 264 (1928).

[12] The authors greatly acknowledge to the help of Mr. Yoshiaki Maruyama and his coworkers, Atomic Research Laboratory, Musashi Institute of Technology, for irradiation.

[13] R. H. Schuler and N. F. Barr, *J. Am. Chem. Soc.*, **78**, 5756 (1956).

[14] The authors are indebted to Mr. Tatsuji Hamada, The Institute of Physical and Chemical Research, for his assistance in β-γ coincidence counting of the irradiated gold foils.

[15] Gold foil data were always higher by about 20%, which might be ascribed to epithermal neutrons.

[16] N. N. Lichtin, *J. Phys. Chem.*, **63**, 1449 (1959).

[17] Correction was made because a small amount of (unidentified) gas usually remained even in the absence of nitrous oxide.

[18] It was reconfirmed that boric acid (up to 0.5 M) does not interfere color development if the concentrated chromotropate solution is used as described in the text.

[19] The "pure" methanol means hereafter the methanol not containing other than trimethyl borate. Trimethyl borate (at least up to 0.5 M) does not affect the γ-radiolysis yields appreciably.

[20] S. U. Choi, N. N. Lichtin and J. J. Rush, *J. Am. Chem. Soc.*, **82**, 3225 (1960).

[21] S. U. Choi and N. N. Lichtin, *ibid.*, **86**, 3948 (1964).

TABLE 1. PRODUCT YIELDS FROM IRRADIATED LIQUID METHANOL WITH THE α, ^{7}Li-RECOILS IN THE PRESENCE AND ABSENCE OF NITROUS OXIDE

No.	Solution		100 eV yield, G						Recoil dose 10^{19} eV/m*l*
	$B(OCH_3)_3$ M	N_2O 10^{-3} M	H_2	CO	CH_4	CH_2O	$C_2H_6O_2$	N_2	
3	0.261	0	6.00	0.95	0.95	2.91	0.50	0	1.66
5	0.267	0	5.26	0.86	0.66	2.89	0.55	0	2.95
8	0.243	0	6.58	1.21	0.81	3.37	—	0	1.64
4	0.264	1.0	5.01	0.80	0.63	2.60	—	0.23	2.91
1	0.303	2.0	6.13	0.97	0.82	3.33	0.42	0.22	1.87
6	0.262	2.8	5.44	0.94	0.77	2.92	—	0.60	2.89
2	0.298	3.6	5.78	0.86	0.65	3.05	0.65	0.25	1.61
7	0.291	5.6	4.12	0.63	0.56	2.20	0.34	0.22	2.74

nitrous oxide. Assuming that nitrous oxide reacts with solvated electrons to produce nitrogen as was assumed in the γ-radiolysis,

$$N_2O + e^-_{solv} \rightarrow N_2 + O^- \; (\rightarrow OH)$$

one could conclude that the yield of the solvated electron in the recoil radiolysis is as low as 0.2, which is only one tenth of that in the γ-radiolysis.

Such a low yield of the solvated electron in the recoil radiolysis may be explained by assuming the recapture process inside tracks. In the dense ionization tracks produced by high LET radiations (*e. g.*, α, ^{7}Li-recoils), electrons will readily be recaptured by parent positive ions before diffusing out of tracks. LET of γ-ray and α, ^{7}Li-recoils in liquid methanol are estimated to be about 0.03 and 30 eV/Å, respectively. Much higher density of ions and electrons in the tracks of recoils results in a markedly reducing separation between them and consequently an increasing probability of electron recapture. The reduced yield of the solvated electron may thus be accounted for.

Assume, in the recoil radiolysis, that $G(H_2)=5.5$, G_{H_2} (molecular hydrogen yield)$=2.4$,²¹⁾ and $G_{e^-_{solv}}=0.2$. If hydrogen is to be produced eventually, as assumed in the γ-radiolysis, by the hydrogen abstraction reaction of H atoms from methanol as well as by molecular process, the hydrogen atom yield in the recoil radiolysis should be $G_H=G(H_2)-H_{H_2}-G_{e^-_{solv}}=2.9$, which is 1.8 times as large as that for the γ-radiolysis ($G_H=1.6$).²²⁾ Choi and Lichtin proposed that, in the recoil radiolysis of oxygenated methanol, long-lived excited methanol molecules diffuse out of tracks and may be quenched by oxygen molecules.²¹⁾ They looked upon these excited molecules as precursors of a part of total hydrogen produced.²¹⁾

As discussed above, it can reasonably be assumed that, in the recoil radiolysis, solvated electrons are readily recaptured before escaping tracks to form excited molecules or hydrogen atoms. If excited methanol has such a long lifetime as to diffuse out of tracks, a reaction toward nitrous oxide in the bulk solution might be expected by analogy of excited water reaction with nitrous oxide.²³⁾ A very low yield of nitrogen and the high G_H obtained above may, therefore, indicate that excited methanol, if any, is not so long-lived but decomposes to form hydrogen atoms inside the track.

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22) In the γ-radiolysis, it is assumed that $G(H_2)=5.4$, $G_{H_2}=1.8$(unpublished result by the present authors) and $G_{e^-_{solv}}=2.0$ (Ref. 6).

23) F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc.* London, **A 267**, 443 (1962); G. V. Buxton and F. S. Dainton, *ibid.*, **A287**, 427 (1965); F. S. Dainton and S. R. Logan, *Trans. Faraday Soc.*, **61**, 715 (1965).