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A New Determination Method of Relative Rate Constants for Reactions with OH-radicals in Radiolysis of Aqueous Solutions[*1]

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Radioactivity of water increased linearly with dose when aqueous solution of ^{3}H-formate (2 μC_i/ml and 2×10^{-3} M) was irradiated with γ-rays in the presence of oxygen. The increase of the radioactivity was found to be reciprocally proportional to the non-labeled formate concentration where the amount of ^{3}H-formate was kept invariable. Addition of ferrocyanide and 2-propanol, effective OH-radicals scavengers, depressed the radioactivity increase to near zero. These facts show that the abstraction of tritium from ^{3}H-formate by OH-radicals causes the increase of the radioactivity of water. A competition method to measure relative rate constants for reactions with OH-radicals was deviced on the present results. Some values obtained by this method were in agreement with published data.

In measuring the relative rate constants for reactions with H atoms, Scholes and Simic[1] have established a competition method in the radiolysis of neutral aqueous systems using deuterioformate as a competitor. Formate undergoes the following reactions (1) and (2) by the attacks of H atoms and OH-radicals, respectively.

Hydrogen deuteride is evolved by the reaction (1) in this method and can be distinguished from the other source evolution of hydrogen.

$$HCO_2^- + H \xrightarrow{K_1} H_2 + CO_2^- \qquad (1)$$

$$HCO_2^- + OH \xrightarrow{K_2} H_2O + CO_2^- \qquad (2)$$

If tritiated formate ($^3HCO_2^-$) is used, H and OH attacks to formate will be indicated by formation of H^3H and H^3HO, respectively. Attempts were made to measure the rate constants for reactions with H and OH by using $^3HCO_2^-$ as a competitor, based

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1) G. Scholes and M. Simic, *J. Phys. Chem.*, **68**, 1738 (1964).

on detections of ^{3}H in H_2 and H_2O in the radiolysis of neutral aqueous solutions. The rate constants for reactions with OH could be readily measured in the presence of oxygen as a reducing species scavenger while those for reactions with H could not be obtained so readily as the former, because of much lower evolution of H^{3}H or much lower increase of radioactivity in the evolved hydrogen.

Experimental

The water used was triply distilled in a continuous Pyrex system (first from alkaline permanganate, second from acidic dichromate, and finally without any additive). Sodium ^{3}H-formate was supplied by the Radiochemical Centre (Amersham, England). Sodium formate, potassium ferrocyanide, sodium nitrite, potassium iodide, methanol, ethanol, 2-propanol, acetone, naphthalene, and dioxane (G. R. grade) were supplied by Kanto Chem. Co., Inc. (Tokyo) and were used as received. PPO (2,5-diphenyloxazole) and POPOP (1,4-bis-2-(5-phenyloxazolyl)-benzene) were Packard scintilater grade.

The stock solution of $^3HCO_2^-$ was 100 μC$_i$/m*l* and 10^{-2} M, and was purified immediately prior to use as follows; to 2—5 m*l* of the stock solution was added 10—20 m*l* of water and the solution was lyophilyzed to dryness. This evaporation was repeated until the sublimed water showed desirably low radioactivity and the final residue of sodium formate was dissolved in water to make up the solution of the original concentration.

Solutions to be irradiated (2.5 m*l*, 20 μC$_i$/m*l*, and 2×10^{-3} M formate) were made up of 0.5 m*l* of the stock solution and 2.0 m*l* water containing solutes tested. Irradiation of the solution was done in 5 m*l* Pyrex tubes (1.5 cm in outer diameter) fitted to standard taper joint covered with plastic film. Irradiation was carried out on ^{60}Co γ-ray source, the dose rate (2.4×10^{16} eV m*l*$^{-1}$ min^{-1}) being determined by the Fricke dosimeter, taking $G(\mathrm{Fe^{III}})=15.6$ and $\varepsilon_{(\mathrm{Fe^{III}})}=2130$ at 305 mμ (22°C).

Prior to measuring radioactivity, water was sublimed under high vacuum from the irradiated solutions and condensed in dry ice-ethanol traps, and was passed through a small column (5—6 mm in diameter and 30—40 mm in length) packed with mixed ion exchangers (Amberlite IR 120-H and Dowex 2-OH, 1 : 1, completely dried at 100°C and stored in desiccator) at the top half and with charcoal (dried at 100°C) at the bottom half. A portion (0.1 m*l*) of the eluate from the column was mixed with 10 m*l* scintillator solution (7 g PPO, 0.3 g POPOP, and 100 g naphthalene in 1 *l* dioxane, 95 parts and water, 5 parts) and the radioactivity was determined on a liquid scintillation counter (Baird-Atomic, Inc., Liquid Scintillation Detector Model 845) at 0°C.

Results and Discussion

When the stock solution of $^3HCO^-_2$ was not purified, the count of the blank sample or the sample not irradiated was extremely high (47404 cpm/0.1 m*l*) as shown in Table 1, and if this sample were irradiated the count increase would not be, therefore, detectable. Three or four times repeated purifications described in the experimental section were required to lower the blank count to desirable level (1145 cpm/0.1 m*l*, after the four repeatings). However, after the purification, rapid increase of the blank count was observed with the lapse of time of the storage or the procedures.

TABLE 1. EFFECTS OF THE PURIFICATION AND THE PRETREATMENT ON BLANK COUNT IN THE MEASUREMENT OF RADIOACTIVITY (cpm/0.1 m*l*)

Repeating of sublimation	Sublimed water	Eluate from ion exchangers	Eluate from ion exchangers and charcoal
1	244358	128044	47404
4	63333	—	1037

This radiochemical impurities may occur from the decomposition of formate by β-radiation of tritium. The series of the procedures including the purification, γ-irradiation, and the measurement of the radioactivity was carried out within the short period of two or three days and the blank sample not irradiated was taken with irradiated one. It was necessary for the measurement of radioactivity to decrease the radioactivity not occurring from the irradiation to low level. For the sake, each of the three components of the pretreatment, sublimation of water, passage through ion exchangers, and passage through charcoal, was indispensable, since the former separated non-volatile materials to prevent the saturation of the latter two adsorbents, and the latter two decreased considerably the blank counts as shown in Table 1.

When the samples containing no additional solute were irradiated under the aerated condition with different doses, 1, 2/3, and $1/3\times 7.2\times 10^{17}$ eV m*l*$^{-1}$, a plot of count *vs.* dose made a straight line as shown in Fig. 1 and *G* (count-increase) was independent of dose. The linearity and the independent *G* (count-increase) suggested that the reaction concerning to the increase of count on irradiation was simple.

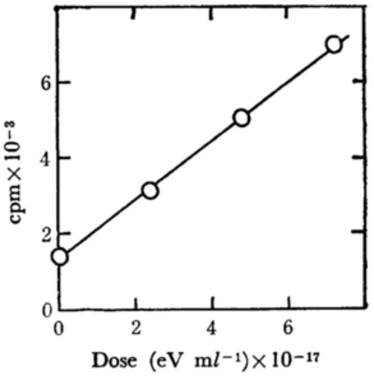

Fig. 1. Plot of count *vs.* dose.

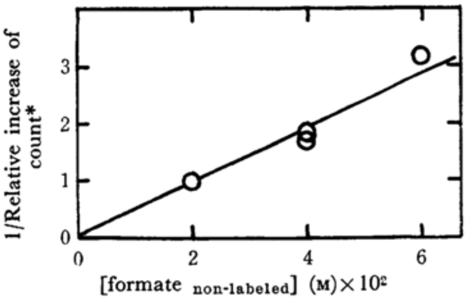

Fig. 2. Reciprocal proportion of count increase to the concentration of non-labeled formate.
* Count increase of the sample without additional non-labeled formate=1.00

Count decreased in reciprocal ratio with increase of the concentration of non-labeled formate, when the dose and the amount of ${}^3HCO_2^-$ were kept invariable, as shown in Fig. 2, in which 1/count-increase *vs.* [$\text{formate}_{\text{non-labeled}}$] was plotted. This reciprocal correlation implies that there is a simple competition between the reaction in which an active species removes tritium from ${}^3HCO_2^-$ to water and that in which the species is scavenged with non-labeled formate. When both ${}^3HCO_2^-$ and HCO_2^- are kept constant, the count increase may be, therefore, proportionate to the amount of the active species scavenged by non-labeled formate.

The count increase is probably caused by OH-radicals attack to ${}^3HCO_2^-$ as in the following reaction.

$$OH + {}^3HCO_2^- \rightarrow H^3HO + CO_2^- \qquad (2')$$

Count increase was effectively depressed to near zero by addition of ferrocyamide or 2-propanol of higher concentration (10^{-1} M) as shown in Table 2. They are known as effective scavengers for OH,[2-4] especially the former is a specific scavenger for OH. This depression of the count increase to near zero with ferrocyanide or 2-propanol may exclude the possibility that secondary species given by the reactions of reducing species, H and e^-_{aq}, with oxygen, HO_2, and O_2^-, contributed to the increase of count, because if these secondary species did so, ferrocyanide or 2-propanol should not reduce the count increase to near zero.

TABLE 2. RADIOACTIVITY IN WATER FROM THE IRRADIATED SOLUTIONS CONTAINING ${}^3HCO_2^-$

Exp. No.	Dose*	Solute added	(M)	Count	Count Increase (cpm/0.1 ml)
1	0	—		1465	—
1	1	—		6975	5510
1	1	$Fe(CN)_6^{4-}$	10^{-1}	1431	−34
2	0	—		1850	—
2	1	*i*-PrOH	10^{-1}	1817	−33

* 7.2×10^{17} eV ml^{-1}

Direct attack of e^-_{aq} to ${}^3HCO^-_2$ seems impossible under the aerated condition, since formate is known to be a poor scavenger for e^-_{aq}, while oxygen is much more effective one. It is calculated from the published datum[5] that the attack of H atoms to formate is decreased by oxygen under this experimental condition to about one tenth.

When 2-propanol was added to the solution in different concentrations, a plot of $\varDelta\text{count}_0/\varDelta\text{count}$ *vs.* [2-propanol]/[formate] is linear as shown in Fig. 3, where count increase is designated as $\varDelta$ count, and $\varDelta$ count_0 is that without 2-propanol added. Assumption that the reaction (2) simply competes the reaction (3),

$$OH + (CH_3)_2CHOH \xrightarrow{K_3} (CH_3)_2\dot{C}OH + H_2O \qquad (3)$$

should lead to the following equation (i),

$$\frac{1}{G(-\text{formate})_{OH}} = \frac{1}{G(OH)}\left(1 + \frac{K_3}{K_2}\,\frac{[\text{2-propanol}]}{[\text{formate}]}\right) \qquad (i)$$

where $G(-\text{formate})_{OH}$ is $G(-\text{formate})$ by the attack of OH.

Moreover, assuming that the count increase is proportionate to the amount of degradation of non-labeled formate with OH, Eq. (i) should be modified as

$$\frac{1}{\varDelta\text{count}} = \frac{1}{\varDelta\text{count}_0}\left(1 + \frac{K_3[\text{2-propanol}]}{K_2[\text{formate}]}\right) \qquad (ii)$$

TABLE 3. RELATIVE RATE CONSTANTS OF SOME SUBSTANCES WITH OH-RADICALS

	this work	published data[4]
formate	1.00	1.00
2-propanol	4.5×10^{-1}	5.3×10^{-1}
ethanol[a]	5.3×10^{-1}	4.6×10^{-1}
methanol[b]	3.0×10^{-1}	2.7×10^{-1}
iodide[c]	3.8	3.6
nitrite[d]	3.0	1-5.2

a) ethanol=5×10^{-3} M and relative increase of count=0.430
b) methanol=8×10^{-3} M and relative increase of count=0.456
c) KI=8×10^{-4} M and relative increase of count=0.394
d) $NaNO_2=10^{-3}$ M and relative increase of count=0.397

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2) J. K. Thomas, *Trans. Faraday Soc.*, **61**, 702 (1965).
3) J. Rabani and G. Stein, *ibid.*, **58**, 2150 (1962).
4) I. Kraljic and C. N. Trumbore, *J. Am. Chem. Soc.*, **87**, 2547 (1965).
5) J. Rabani, *J. Phys. Chem.*, **66**, 361 (1962).

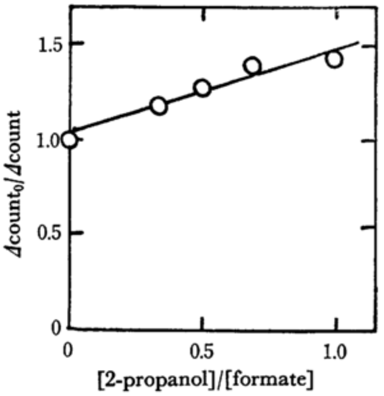
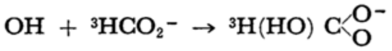


Fig. 3. Test of simple competition for OH radicals between formate and 2-propanol.

The slope of the straight line in Fig. 3 or the relative rate constant, $K=K_{(2\text{-propanol}+\text{OH})}/K_{(\text{formate}+\text{OH})}=0.45$, is in agreement with a published value, 0.53.[4]

The relative constants of ethanol, methanol, iodide, and nitrite were also calculated from data at each one concentration point and the listed in Table 3. They agree with published data, except the rate constant of nitrite, which has been reported as widely varied values, for the reactivity of nitrite to OH-radicals may markedly depend on pH.

In addition to the abstraction reaction (2′), an addition reaction of OH-radicals to $^3HCO_2^-$ may occur as in the reaction (4).



$$OH + {}^3HCO_2^- \rightarrow {}^3H(HO)\,C\begin{matrix}\diagup O^- \\ \diagdown O\end{matrix} \qquad (4)$$

When the other solute capable to scavenge OH is added to the system, the reaction (4) as well as (2′) will be depressed by simple competition for OH. Formation of H^3HO from the radical ion given by the reaction (4) will be, however, complicatedly influenced from the active species produced by the reactions concerning to the added solute. If the reaction (4) were not negligible in comparison with (2′), the total yield of H^3HO would not, therefore, obey simple competition rule in the presence of other solute. Results in Fig. 3 and Table 3 suggest that the reaction (4) may not, at least, be important, similarly as addition reaction in non-labeled formate may not be.[6-8]

The accuracy of this method is limited mainly by the error in the liquid scintillation counter measurement. The error seems to occur from the variation of counting efficiency by the incomplete stabilization of temperature. Consequently, the accuracy will be much more improved if the measurement is carried out on a counter set at more stabilized temperature.

We are indebted to Mr. Shinkichi Katsura for the operation of irradiation.

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6) E. J. Hart, *J. Am. Chem. Soc.*, **73**, 68 (1951).
7) E. J. Hart, *ibid.*, **76**, 4198 (1954).
8) E. J. Hart, *ibid.*, **76**,, 4312 (1954).