RADIOLYSIS OF METHANOL BY RECOILS FROM THE B^{10} (n,α)Li^7 REACTION[1]

Sir:

The radiolysis of methanol has been the subject of much recent work.[2] Only one[2b] of these studies employed alpha particles. McDonell and Newton's work utilized 28 mev. cyclotron alphas, involved destruction of about 2% of the substrate and was carried out before the difficulty in achieving reproducibility in this system was recognized.

The work reported herein employed the alpha and Li^7 recoils of total energy 2.35 mev. per nuclear event resulting from the absorption of thermal neutrons by boron present in the form of dissolved methyl borate. Liquid methanol which was approximately 0.2 M in methyl borate was irradiated in the thermal-neutron facility[3] of the Brookhaven National Laboratory. Total energy absorbed from alpha particles was determined in two ways. In Method I, dosimeters consisting of aerated 0.001 M $FeSO_4$ in 0.8 N aqueous sulfuric acid containing 0.149 M boric acid were used in conjunction with the value of $G(Fe^{+3}) = 4.22$ determined by Schuler and Barr[4] for boron recoils in this system. Gamma background was determined simultaneously with boron-free Fricke dosimeters taking $G(Fe^{+3}) = 15.6$. It was assumed that the entire alpha plus lithium flux is absorbed in both the dosimeter solution and in methanol. No correction was applied for the gamma energy associated with alpha emission. Method II employed a scintillation counter calibrated by β-γ-coincidence counting of simultaneously neutron-irradiated gold foils.[4,5] After correction for attenuation of the neutron flux by boron,[4] the latter procedure yielded values that exceeded by about 7% those provided by Method I. The results of Method I were employed in calculating the G-values presented in Table I.

TABLE I

Energy source	Product yields, molecules/100 ev. H_2	CO	CH_4	CH_2O	$(CH_2OH)_2$
2.35 Mev. recoils[a]	5.14 ± 0.02	0.92 ± 0.06	0.67 ± 0.04	3.45 ± 0.10	1.40 ± 0.10
Co^{60} gamma[b]	4.40 ± 0.01	0.07 ± 0.01	0.31 ± 0.06	2.86 ± 0.17	2.85 ± 0.08

[a] Uncertainties are av. deviations from the mean of results of four radiolyses. [b] Two radiolyses in the presence of *ca.* 0.2 M methyl borate.

The methanol was Fisher's "Certified Reagent" which was purified, degassed and charged into quartz irradiation cells in essentially the same fashion as has already been described.[2h] Trimethyl borate (Metal Hydrides Co.) was purified by distillation using a 40 cm. column packed with glass helices. In the runs which provided the data of Table I, its concentration fell in the range 0.170 to 0.268M. Analytical procedures were similar to those that have already been described.[2h] Preliminary work[6] established that borate does not interfere with determination of ethylene glycol with the aid of chromotropic acid,[2h] but does interfere with determination of formaldehyde unless an increased amount of chromotropic acid (1 ml. of 25% solution) is employed.

The Saunders–Taylor micromanometric analysis was improved by use of CuO containing 1.3% of Fe_2O_3 which was prepared according to the method of Brückner and Schick[7] and was validated by analysis of known mixtures. Yields obtained in Co^{60} gamma radiolysis of methanol containing approx. 0.2 M methyl borate are also presented in Table I and were used in correcting for radiolysis by the gamma background present in the thermal column. Total recoil doses were about 3×10^{19} ev./ml.; gamma energy absorbed was about 7×10^{17} ev./ml. About 0.02% of the methanol was decomposed in the recoil radiolyses.

The data of Table I must be considered with caution in view of the uncertainty which still exists as to $G(H_2)$ and $G(CH_4)$ for Co^{60} gamma radiolysis of "pure" methanol. Borate appears to have little effect on $G(CH_4)$, $G(CO)$ and $G(C_2H_6O_2)$ of gamma radiolysis but appears to increase $G(CH_2O)$ significantly and probably reduces $G(H_2)$. The much greater LET of the recoil radiolysis as compared to gamma radiolysis has these consequences:

(1) $G(-CH_3OH)$ is somewhat *increased*
(2) $G(CO)$ increases at least tenfold and $G(CH_4)$ about twofold
(3) $G(C_2H_6O_2)$ is halved and the loss is only partially compensated by increase in $G(CH_2O)$

In the presence of 0.2 M borate, $G(Ox)$ exceeds $G(Red)$ by about 1 for both gamma ray and recoil particle radiolyses. The formation of an as yet unidentified reduction product or products is thereby suggested.

---

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission, in part under Contract AT (30-1) 2383.

(2) (a) W. J. Skraba, J. C. Burr, Jr., and D. N. Hess, *J. Chem. Phys.*, **21**, 1296 (1953); (b) W. R. McDonell and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954); (c) W. R. McDonell and S. Gordon, *J. Chem. Phys.*, **23**, 208 (1955); (d) W. R. McDonell, *ibid.*, **23**, 208 (1955); (e) G. Meshitsuka, K. Ouchi, K. Hirota and G. Kusumoto, *J. Chem. Soc. Japan*, **78**, 129 (1957); (f) G. Meshitsuka and M. Burton, *Radiation Research*, **8**, 285 (1958); (g) G. E. Adams and J. H. Baxendale, THIS JOURNAL, **80**, 4125 (1958); (h) N. N. Lichtin, *J. Phys. Chem.*, **63**, 1449 (1959).

(3) H. J. Curtis, S. R. Person, F. B. Oleson, J. E. Henkel and N. Delihas, *Nucleonics*, **14**, No. 2, 26 (1956).

(4) R. H. Schuler and N. F. Barr, THIS JOURNAL, **78**, 5756 (1956).

(5) H. H. Seliger and A. Schwebel, *Nucleonics*, **12**, No. 7, 54 (1954).

(6) Carried out by Miss B. Dudek under the sponsorship of a grant of the National Science Foundation's undergraduate research participation program.

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

CHEMISTRY DEPARTMENT SANG UP CHOI
BOSTON UNIVERSITY NORMAN N. LICHTIN
BOSTON, MASS.
CHEMISTRY DEPARTMENT JOHN J. RUSH
BROOKHAVEN NATIONAL LABORATORY
UPTON, L. I., N. Y.

RECEIVED APRIL 22, 1960

THE STRUCTURE OF OLEANDOMYCIN

Sir:

Oleandomycin, I, $C_{35}H_{61}NO_{12}$, is a macrolide antibiotic[1] which has been shown to contain the deoxysugars desosamine and L-oleandrose, glycosidically linked to a lactonic aglycone which possesses hy-

---

(1) This antibiotic, in the form of its triacetate ester, is known by the name Tao, a registered trade mark of Chas. Pfizer and Co., Inc.