## RADIOLYSIS OF METHANOL BY RECOILS FROM THE $B^{10}(n,\alpha)Li^7$ REACTION<sup>1</sup>

Sir:

The radiolysis of methanol has been the subject of much recent work.<sup>2</sup> Only one<sup>2b</sup> 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<sup>7</sup> 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 facility3 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<sup>4</sup> 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 solu0.268M. Analytical procedures were similar to those that have already been described.<sup>2h</sup> Preliminary work<sup>6</sup> established that borate does not interfere with determination of ethylene glycol with the aid of chromotropic acid,<sup>2h</sup> 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<sub>2</sub>O<sub>3</sub> which was prepared according to the method of Brückner and Schick<sup>7</sup> and was validated by analysis of known mixtures. Yields obtained in Co<sup>60</sup> 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  $3 \times 10^{19}$ ev./ml.; gamma energy absorbed was about  $7 \times 10^{17}$  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<sup>60</sup> 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

## Table I

Energy	Product yields. molecules/100 ev.				
source	$H_2$	CO	CH4	CH2O	$(CH_2OH)_2$
2.35 Mev. recoils*	$5.14 \pm 0.02$	$0.92 \pm 0.06$	$0.67 \pm 0.04$	$3.45 \pm 0.10$	$1.40 \pm 0.10$
Co <sup>60</sup> gamma <sup>b</sup>	$4.40 \pm 0.01$	$0.07 \pm 0.01$	$0.31 \pm 0.06$	$2.86 \pm 0.17$	$2.85 \pm 0.08$
" Uncertainties are av.	deviations from the	e mean of results o	of four radiolyses.	<sup>b</sup> Two radiolyses ir	the presence of ca-

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0.2 M methyl borate.

tion and in methanol. No correction was applied for the gamma energy associated with alpha emission. Method II employed a scintillation counter calibrated by  $\beta$ - $\gamma$ -coincidence counting of simultaneously neutron-irradiated gold foils.<sup>4,5</sup> After correction for attenuation of the neutron flux by boron,<sup>4</sup> 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.

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.<sup>2h</sup> 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

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

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(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).

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)  $G(C_{2}H_{6}O_{2})$  is halved and the loss is only partially compensated by increase in  $G(CH_{2}O)$

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.

(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

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## THE STRUCTURE OF OLEANDOMYCIN

Oleandomycin, I,  $C_{85}H_{61}NO_{12}$ , is a macrolide antibiotic<sup>1</sup> 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.