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THE REACTIONS OF ENERGETIC CARBON ATOMS IN METHANE;
OXYGEN AND PHASE DEPENDENCE; RADIATION DAMAGE EFFECTS¹

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The reactions of energetic carbon-11 species impinging on a gaseous system comprised of 2% oxygen and 98% methane have been described by MacKay and Wolfgang.⁴ The oxygen was added to "minimize radiation induced reduction of unsaturated hydrocarbon products and to act as a scavenger for carbon atoms⁴". Results for oxygen free methane were not reported since erratic amounts of CO were obtained. A similar difficulty, while not apparent in the case of higher homologous hydrocarbons studied by the same authors,^{5,6} was experienced in a study of the $C^{11} + H_2$ system, in which system a possible wall oxidation effect was suggested.⁵

In order to gain more information on the methane system we have continued the study of methane, varying a variety of chemical and physical parameters. We have used the nuclear reactions $C^{12}(n,2n)C^{11}$ and $C^{12}(p,pn)C^{11}$ to produce the carbon-11.

Experimental

Purification of Methane.—Traces of CO_2 were removed from the methane (Phillips Research Grade) by passing the methane through Ascarite. The gas was then transferred to a 500 c.c. stainless steel oven containing calcium

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turnings (previously degassed at room temperature; 24 hrs. pumping at 10^{-5} mm. Hg; temperature raised to 350°C ; baked at 350°C for 3 days while pumping). The oven, containing CH_4 , was closed to the line and kept at 350°C for 15 min. This procedure reduced the oxygen content from 100-200 ppm. (O_2 content of our Phillips methane sample) to below 10 ppm. (limit of assay method) of O_2 . The N_2 , normally at 200 ppm., was reduced to 50 ppm.

Miscellaneous Compounds.—The acetylene and ethylene used were Matheson, C.P. grade. Each gas was purified by multiple crystallization. The oxygen (Matheson, C.P. grade) was used without further purification.

Irradiation Techniques.—The experimental irradiation technique for the $\text{C}^{12}(\text{n},2\text{n})\text{C}^{11}$ reaction was essentially that described by Suryanarayana and Wolf.⁷ The induced specific activities ranged from 3000-6000 dpm./cc. methane at NTP. The tank material was quartz.

The Brookhaven Cosmotron was used for the $\text{C}^{12}(\text{p},\text{pn})\text{C}^{11}$ reaction. Proton energies of 2-3 GeV were used at intensities of 10^{10} - 10^{11} protons per pulse (12/min.) in an external beam. The irradiation cylinder was 2S aluminum, 200 mm. ϕ x 40 mm. i.d. The cylinder was lined up with the beam by taking a picture of the beam (Polaroid film) at both ends of the tank using one pulse to expose the film. Details of the shadow cast by the tank in the developed film allowed simple correction of alignment. The total activity induced in the gas was compared with that induced in polyethylene foils⁸ held at both ends of the tank during the run, appropriate corrections for C^{11} loss from the foil being made first. In all cases, using methane, we found 95+% of the activity produced (using the foil as the absolute monitor) to be in the gas phase. The specific activities were 2000-4000 dpm./cc. methane at NTP.

The total activity cannot be assayed directly when using the n,2n reaction. However, in all cases studied, the activity produced was proportional to the integrated value for the deuterons impinging on the LiH target. The fact that nearly all the carbon-11 activity produced by the p,pn reaction is found in the gas coupled with the fact that product distributions were identical at the same doses for the two nuclear reactions, leads us to suggest that 95-100% of the activity is also recovered in the gas phase when using the n,2n reaction.

Dosimetry.—Dose measurements were made using conventional ferrous sulfate dosimetry. The carbon-11 activity ^{per} accompanying dose in dpm./mg.C per ev./molecule is $\sim 6 \times 10^6$ for the n,2n reaction and $\sim 5 \times 10^7$ for the p,pn reaction. The methane received 10^{-4} - 10^{-3} ev./molecule in most runs. (See also Table I)

Activity Assay and Compound Identification.—The compounds produced were identified and the activities measured by a combination of GLC and gas phase effluent counting.⁹ The columns used in this work were; 1. 1.5 m. x 5 mm. i.d. glass column, containing activated carbon (Columbia Carbon Corp.); 2. 3 m. x 5 mm. i.d. glass column, containing activated alumina coated with 0.5% Dow Corning Silicone-550 (Burrell Corp.); 3. 2.3 m. x 5 mm. i.d. glass column containing 13 X molecular sieve (Burrell Corp.); and 4. 10 m. x 4 mm. i.d. glass column containing 20% dimethylsulfolane on 60-80 mesh acid-washed firebrick. Column temperatures were 18-20°C. The columns were attached to a single manifold allowing rapid switch-over during successive runs.

The specific activity of the irradiated gas was determined by bypassing the columns and sending an aliquot directly through our effluent window counter. In some instances static internal proportional counting of an aliquot from the tank was carried out.

Table I

ref. 9

The Effect of Dose and Scavenger

Concomitant radiolysis of the methane during carbon-11 production clearly affects product distribution (Table I). A factor of two in absorbed dose produces an increase in ethane-C¹¹ yield and an even greater increase in propane-C¹¹ yield. The yields of methane, ethylene and acetylene are seen to decrease. Several mechanisms are probably operative.

The most probable mechanism for propane formation in our view is outlined by eqs. 1-4

In this mechanism the ethylene-C¹¹ scavenges a radiolytically produced hydrogen atom, the resultant radical then reacting with a radiolytically produced methyl radical. An alternative to this mechanism involving reaction of ethylene-C¹¹ with a methyl radical and then a reaction with a hydrogen atom cannot be distinguished from the mechanism given by eqs. 1-4 under our conditions. A third mechanism, which might account for the major portion of the propane-C¹¹, involving the scavenging of methyl-C¹¹ radicals by radiolytically produced ethylene is ruled out by the data in column 4, Table II. The addition of scavenger ethylene¹⁰ would be expected to lead to an unchanged yield of propane-C¹¹ or perhaps to enhance it slightly (efficient scavenging of C¹¹H₃·) if this mechanism were operative. The appreciable drop observed in the propane-C¹¹ yield is inconsistent with the consequences of mechanism three but in support of mechanism one (and its alternative).

Table II
ref. 10

The mechanism of ethane- C^{11} formation can also be understood in terms of the reactions of the accompanying radiolytically and recoil produced species. It cannot arise from methyl radical recombination ($C^{11}H_3\cdot + CH_3\cdot$) since the addition of olefin scavengers reduces the ethane- C^{11} yield, from 23.9% to 3.4% for 1.2% of added ethylene, and to 6.0% for 2.0% of added acetylene. (ethylene is a good methyl radical scavenger and we should therefore expect an enhanced yield of propene- C^{11} and propane- C^{11}). With added oxygen the ethane- C^{11} yield drops from 23.9% to less than 0.5%.

Oxygen is a good alkyl radical trap and hydrogen atom trap. It can also react with such things as triplet "radicals" but its efficiency is probably not as great in this case.¹¹

ref. 11

The ethylene- C^{11} yield drops from a maximum of 30.5% when 0.12% O_2 is present to 12.4% when no oxygen is in the system. The yield of acetylene- C^{11} can also be seen to drop when comparing the scavenged and unscavenged system.⁵ In the unscavenged system reduction by hydrogen atoms is probably occurring (MacKay and Wolfgang⁴ have suggested hydrogen atoms as reducing agents in these systems). It is unlikely however that all of the ethane- C^{11} and propane- C^{11} observed in the unscavenged system is formed by reduction.

ref. 12

Part of the ethane- C^{11} may be formed by methylene- C^{11} insertion (cf. reference 12). When using ethylene scavenger, the methylene insertion products, ethane- C^{11} and cyclopropane- $C^{11,12}$ account for 6.2% of the carbon-11 produced. Added acetylene allows a 6% yield of ethane- C^{11} to be formed. The presumed cyclopropene- C^{11} , if formed at all, would not be detected under our conditions.

The data are at least in qualitative agreement with the hypothesis that ethane- C^{11} formation in unscavenged methane is caused primarily by hydrogen

atom reduction of ethylene- C^{11} and by methylene- C^{11} insertion reactions.

In the case of the reaction of energetic carbon in the methane system, no significant oxidation of the carbon-11 occurs at the walls since the absence of gaseous oxygen in the methane eliminates the appearance of CO. Further it is unlikely that the wall is acting as a third body since, 1) the gas pressure is one atm., 2) the geometry of our reaction vessels and their materials of construction are quite different in different experiments; and yet no effect is observed in product distribution at comparable absorbed doses.

Fig. 1

The addition of oxygen (data plotted in Fig. 1) essentially eliminates methane- C^{11} , ethane- C^{11} and propane- C^{11} (cf. columns 1 and 2, Table II).

Oxygen can react as a scavenger for hydrogen atoms, as suggested by MacKay and Wolfgang, but it is also reacting as a general radical scavenger.

Furthermore in view of the marked dependence of product distribution on varying oxygen concentration it seems reasonable to assume that the oxygen may also be reacting with non-thermal and excited species.

ref. 13

The effect of oxygen can be summarized as follows: 1) the elimination of the radiolytically produced species which transform part of the "primary" recoil products (e.g. stabilized C_2H_2 and C_2H_4) to other compounds thereby causing an initial rise¹³ in the yield of acetylene- C^{11} and ethylene- C^{11} , 2) the reaction of oxygen with energetic carbon atoms and with some of the precursors of the observed products resulting in a continual decrease of acetylene, ethylene and other products as the oxygen concentration is increased. This effect reflects the competition of oxygen with the substrate for the precursors involved (cf. curves Fig. 1).

The effect of added acetylene (column 3, Table II) is self protective in nature, the yield of acetylene and ethylene going up as in the case of added oxygen. Apparently acetylene is not as reactive as ethylene in interfering with some of the other reactions going on.

The Effect of Phase

If one considers the yield of acetylene and ethylene to be indicative of the amount of radiation damage the system receives during carbon-11 formation, in the sense that the yields of these products at relatively low oxygen concentrations (where the curves, Fig. 1, are at their maximum) are those to be expected when no radiation is present (i.e. when only energetic carbon atoms are introduced), then it can be suggested that there is little dose effect in the solid. However, it also can be seen (column 5, Table II) that sizable yields of products eliminated in the gas phase by oxygen do appear in the solid, e.g. methane, ethane and propane ($\Sigma = 20.3\%$). Consequently it is unlikely that the ethane formed in the solid phase irradiation is produced by the reduction of ethylene (i.e. $C_2H_4 + O_2g = 30\%$, $C_2H_4^l = 28\%$). In the gas phase in the absence of O_2 it is probable that at least some of the ethane is formed in this way. In the solid phase a large fraction of the ethane is probably formed by methylene- C^{11} insertion into methane.¹⁴

ref. 14

The pronounced phase effect leading to decreased ethylene and acetylene yields observed in ethane and propane (cf. reference given in footnote 14) is not apparent here. This may be a reflection of the relative inability of methane, because of its limited number of degrees of freedom, to deexcite the energetic intermediates which lead to acetylene and ethylene. Their formation is thus relatively unhindered, sufficient energy being available in the complex for the requisite bond rupture and rearrangement processes.

The Effect of the Type of Nuclear Reaction

In all cases, in duplicate systems, the product distributions resulting from inducing the $C^{12}(p,pn)C^{11}$ reaction were the same within experimental error as those resulting from the $C^{12}(n,2n)C^{11}$ reaction. We therefore felt it superfluous to include product data from the $C^{12}(p,pn)C^{11}$ runs. Nevertheless the use of these two nuclear processes allowed us to cross check the effect of such parameters as varying radiation intensity and type of radiation, the effect of irradiation vessel materials and such other parameters as might be thought to have an effect on the results. In addition it provides another case where the initial recoil energy of the reactive fragment has no bearing on the product distribution observed. The maximum recoil energy for the $C^{12}(n,2n)C^{11}$ process is 1.1 MeV, whereas the mean recoil energy¹⁵ for the $C^{12}(p,pn)C^{11}$ process is ~ 1.8 MeV.

ref. 15

Table I

Dose Dependence in Methane (n,2n)

	4.8×10^{-4} ev./molecule	8.3×10^{-4} ev./molecule
CO	--- ^a	--- ^a
CH ₄	13.9 $\pm$ 2.2	6.9 $\pm$ 0.5
C ₂ H ₂	17.7 $\pm$ 1.4	14.0 $\pm$ 0.7
C ₂ H ₄	12.4 $\pm$ 1.1	6.6 $\pm$ 0.6
C ₂ H ₆	23.9 $\pm$ 2.0	29.4 $\pm$ 0.6
C ₃ H ₈	11.2 $\pm$ 2.3	20.2 $\pm$ 0.6
allene	3.0 $\pm$ 1.0	---
higher boiling	17.9	22.9

^a Below detectable limit of $\sim 0.2\%$.

Table II

Scavenger and Phase Dependence of Product Distribution in the Carbon-11

Recoil Products in Methane $[C^{12}(n,2n)C^{11}]$ Yields in Percent of Total Carbon-11 in Gas Phase^a

	0.00% O ₂	0.12% O ₂ ^b	2.0% C ₂ H ₂	1.2% C ₂ H ₄	Solid CH ₄ glass at -196°C
CO	--- ^c	20.4 ± 3.1 ^d	--- ^c	--- ^c	--- ^c
CH ₄	13.9 ± 2.2 ^d	<0.15	1.9	--- ^c	4.5
C ₂ H ₂	17.7 ± 1.4	32.3 ± 2.3	32.8	25.2 ± 0.1 ^d	28.1
C ₂ H ₄	12.4 ± 1.1	30.5 ± 0.3	29.5	23.5 ± 0.6	27.2
C ₂ H ₆	23.9 ± 2.0	<0.5	6.0	3.4 ± 0.1	11.3
C ₃ H ₈	11.1 ± 2.3	--- ^c	--- ^c	1.7 ± 0.2	4.5
allene	3.0 ± 1.0	<1.0	--- ^c	--- ^c	--- ^c
higher boiling	17.9	15.8 ^e	29.8	57.7 ^f	24.4

^a Approximate absorbed dose for these runs = $4\lambda 5 \times 10^{-4}$ ev./molecule. Irradiation time = 40 min. Gases at 1 ATM. Concentration in vol. % at NTP. Solid methane was flash evaporated.

^b Oxygen concentration at which we observe the maximum C₂¹¹H₂ and C₂¹¹H₄ yields.

^c Below detectable limit of ~0.2%.

^d A. D. of replicate runs.

^e The average yield of all higher boiling products of all other methane-oxygen mixtures studied (given in Fig. 1) is 18.4 ± 1.7 . At all oxygen concentrations above 2% we observed a 2% yield of CH₃OH also.

^f The yield of cyclopropane is 2.8 ± 0.7 and the yield of propene is 1.5 ± 0.3 . Isobutane, ⁿ-butane, butene-1, i-butylene and propyne are all present but each in yields less than 1%. We were unfortunately unable to analyze for C₅-hydrocarbons. One might expect a fair yield of these compounds.

- (1) Work performed under the auspices of the U. S. Atomic Energy Commission.
- (2) Research Associate, BNL, 1959-61. Current address, Euratom, Ispra, Varese, Italy.
- (3) Requests for reprints should be directed to this author.
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- (10) In the high conversion radiolysis of methane using ethylene- C^{14} as a scavenger, F. Schmidt-Bleck, M. Kayama and F. S. Rowland, University of Kansas (private communication) find the main products to be $C_2^{14}H_6$ and $C_3^{14}H_8$. Their system is also very sensitive to oxygen.
- (11) D. W. Setser, D. W. Placzek, R. J. Cvetanović and B. S. Rabinovitch, Can. J. Chem., 40, 2179 (1962).
- (12) The ratio of propene- C^{11} to cyclopropane- C^{11} is ≈ 0.53 . This ratio is comparable to what was found for the butenes/methylcyclopropane ratio when propylene and methylene (from ketene) were allowed to react at ~ 1 atm. total pressure [J. N. Butler and G. B. Kistiakowsky, J. Am. Chem. Soc., 82, 759 (1962)]. Nothing more than a qualitative comparison with the work of Butler and Kistiakowsky (energy of CH_2 ·, energy of the adduct, ratios, etc.) is possible here because of the error limits of our ratios.

- (13) The systems ethane-oxygen and propane-oxygen (paper in preparation) do not show this rise at any oxygen concentration we were able to achieve. It is possible that a self-protective effect (e.g. such as radiolytically induced olefin formation, i.e. in situ scavenger production) may be operating here.
- (14) The yields of the presumed methylene insertion products (e.g. $C^{11}H_2 + CH_4 \rightarrow C^{11}H_3-CH_3$) in condensed phases is curiously constant in three systems, being 11.3% in methane, 11.5% in ethane and 12.1% in propane. (Ethane and propane reactions are discussed by G. Stöcklin and A. P. Wolf, J. Am. Chem. Soc., in press.) This would suggest that the formation of $C^{11}H_2$ is independent of the compound being irradiated in a homologous series of this sort, a fixed fraction being formed and then reacting in a statistical way with the substrate.
- (15) S. Singh and J. M. Alexander, University of California Lawrence Radiation Laboratory Report, UCRL-9911, October 24, 1961.

Fig. 1. Oxygen dependence of acetylene- C^{11} and ethylene- C^{11} .

FIGURE 1