This can be explained by the $4n + 2$ property of the tropylium ring, which has a high affinity to retain six π electrons. Because of the excessive π electrons in this dianion relative to VIII, and the inability of the COT ring to accommodate both the two extra electrons, charges are forced to migrate back and forth from one tropylium ring to the other, *via* the central COT unit. Hence, this dianion would be very unstable, if it exists at all.

Conclusion

Several general trends can be drawn in these eight-membered ring compounds.

1. By fusion of a benzo group to a COT ring, the bond length of the shared bond will remain benzenoidal in character (1.4 Å).
2. Any system, which possesses an "octalene-like 14 π-electron" unit, will have a long central cross-linkage (1.49 Å) which favors the stability of a $4n + 2$ moiety (for example, bond *e* in III, IV, and VII).
3. Any composite unit of seven- or eight-membered rings that gains or loses π electrons toward the $4n + 2$ limit will stabilize the whole molecule. Thus the stabilization energy of COT dianion, I^{2-}, is higher than that of COT (I); IV^- > octalene (III); *sym*-dibenzocyclooctatetraene dianion (V^{2-}) > V; and $VIII^{2+}$ > VIII.

The ease with which these hydrocarbons are reduced is explained in a similar manner by the SECC values.

Acknowledgments. The authors wish to thank the National Research Council of Canada (NRC) for support of this research. One of us (D. H. L.) wishes to thank Canadian Industries Ltd. for the award of a fellowship (1967–1968), and NRC for the award of a scholarship (1968–1969).

Reactions of Recoil Carbon Atoms in Methanol and Ethanol[1a]

Gerard F. Palino[1b] and Adolf F. Voigt

Contribution from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010. Received July 8, 1968

Abstract: Carbon-11 was produced by the reaction $^{12}C(\gamma,n)^{11}C$ in liquid methanol and ethanol, and the labeled products were separated and determined by radio-gas chromatography. A wide variety of products was observed from both alcohols. In the case of methanol mechanisms are proposed for their formation on the basis of the effect of change in dose and presence of I_2 or DPPH scavenger. Without scavenger many products result from reaction of the ^{11}C-containing intermediates with radicals observed in the radiation chemistry of methanol, particularly the hydroxy methyl radical, the hydrogen atom, and the solvated electron. Iodine scavenger effectively removes these radicals, and the product distribution can be explained on the basis of reactions of ^{11}C, ^{11}CH, and $^{11}CH_2$ with the C–H and O–H bonds and of ^{11}C with a lone electron pair on oxygen. Iodine enters the reaction path by competition with the radiation-produced radicals, removing them and in their place reacting with the ^{11}C-containing intermediates. In several cases the products of these reactions react further with methanol to produce dialkoxyalkanes. The study of the ethanol system was less intensive; mechanisms proposed for this system are similar to those for methanol.

The study of the recoil chemistry of atomic carbon has received considerable attention in recent years and several reviews have appeared.[2,3] In general, the observed chemistry in the simple hydrocarbons can be successfully interpreted in terms of the insertion reactions into C—H and C=C molecular bonds by energetic carbon atoms, methyne, and methylene. The subsequent reactions of the resultant adducts depend upon factors such as their internal energy and the phase and chemical composition of their environment.

Relatively little information is available on the reactions of recoil carbon with other functional groups in organic systems. Cacace, *et al.*,[4] in a recent study of methylamine, indicated that the C–H bond was more reactive toward insertion reactions than was the N–H bond. Attack of atomic carbon at the oxygen atom in ethylene oxide was postulated by MacKay and Wolfgang[5] to account for the observed high yield of ^{11}CO. Oae, *et al.*,[6] have reported on the reactions of ^{14}C in the system methanol–ammonia under reactor irradiation, presenting the yields of saturated C_1 to C_5 alcohols and the results of degradation studies on the ethanol and 1-propanol fractions.

In the reactions of vapor-deposited carbon atoms with alcohols, dialkoxymethanes are formed as the major products.[7,8] Deoxygenation with formation of carbon monoxide was observed to occur with ketones, ethers, and epoxides, but was not observed with water and the simple alcohols.[9]

This study was undertaken to supply information on the reactions of recoil or atomic carbon with organic molecules containing the hydroxyl, alkoxyl, and carbonyl functional groups. The paper describes the

---

(1) (a) Work was performed at the Ames Laboratory of the U. S. Atomic Energy Commission, Contribution No. 2348; (b) based on part of the Ph.D. thesis submitted by Gerard F. Palino to Iowa State University.

(2) A. P. Wolf, *Advan. Phys. Org. Chem.*, 2, 201 (1964).

(3) R. Wolfgang, *Progr. Reaction Kinetics*, 3, 97 (1965).

(4) F. Cacace, G. Stoecklin, and A. P. Wolf, *Radiochim. Acta*, 5, 155 (1966).

(5) C. MacKay and R. Wolfgang, *ibid.*, 1, 42 (1962).

(6) S. Oae, C. S. Redvanly, and A. P. Wolf, *J. Labelled Compds.*, 4, 28 (1968).

(7) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, 87, 1135 (1965).

(8) P. S. Skell and R. F. Harris, *ibid.*, 88, 5933 (1966).

(9) P. S. Skell, J. H. Plonka, and R. R. Engel, *ibid.*, 89, 1748 (1967).

investigation of the reactions of ^{11}C with liquid methanol and ethanol, chosen because they are the simplest organic molecules containing the hydroxyl group. A study of the complete product spectrum was attempted and the effects of changes in dose and of the presence of iodine as scavenger were measured. Relationships were established between a number of products whose yield depends on dose and scavenger.

Experimental Section

Materials. Methanol (Fisher Certified Reagent) and ethanol (Commercial Solvents Corp.) with stated purities of 99.9+ mole % were treated to remove traces of aldehydes and ketones.[10] The methanol was dried by reaction with magnesium methoxide[11] and the ethanol was dried with Molecular Sieve 4A (Linde Co.) using an apparatus and technique similar to that described by Arthur, *et al.*[12] During drying and distillation steps, the apparatus was protected at all times from atmospheric moisture. The unscavenged samples were prepared by vacuum distillation of the degassed solvent into Pyrex sample bulblets 8.6 mm in diameter. The scavenged solutions were prepared by quickly adding the solvent to volumetric flasks containing the appropriate weight of iodine (Baker Analyzed) or 2,2-diphenyl-1-picrylhydrazyl, DPPH (Eastman Organic Chemicals). Iodine was soluble over the concentration range studied, but a solution of methanol prepared to 10^{-3} *M* DPPH contained some undissolved solute. The scavenged samples were prepared by pipeting these solutions through a rubber septum into the sample bulblets, degassing and sealing under vacuum. During the preparation of these samples, the alcohols were exposed to atmospheric moisture for short periods of time. No evidence of detectable impurities was found when the solvents were analyzed by gas chromatography.

Research grade isopentane (Phillips Petroleum Co.) had a stated purity of 99.99 mole % and was used without further purification, the samples being prepared by the pipeting technique.

Production of Atomic Carbon. Free atoms of ^{11}C are produced *in situ* by the nuclear reaction, $^{12}C(\gamma,n)^{11}C$l, using the bremsstrahlung beam from a General Electric Model M electron synchrotron operating at a maximum energy of 70 MeV. The techniques used in these irradiations were described in a previous paper.[13] Although probably initially charged, the ^{11}C atoms are neutral when they reach the energy for chemical reaction. Their distribution among electronic excitation states is not known, but the ground ^3P state and the first two excited states, ^1D and ^1S at 1.3 and 2.7 eV, are the most likely states in these solvents as has been postulated for hydrocarbons.[3]

Separation and Detection. Separation of the radioactive products was performed on an F&M research chromatograph, Model 810R, which was modified to facilitate the analyses required in this work. A brief description of the major modifications follows. The instrument was commercially equipped with both a gas-sampling valve and syringe injection port. To facilitate the on-column injection of a large sample, a sample breaker was installed between the syringe injection port and column connection. This breaker was insulated from the chromatograph oven and heated with a 250-W heater controlled by one of the chromatograph electronic circuits. The injection configuration allowed the simultaneous operation of the three injection systems as well as independent operation of each. This condition is desirable when gaseous or liquid carriers are added for column reactivity studies or for product identification.

The detection system for the radioactive effluent consisted of a 7.5 × 7.5 cm NaI (Tl) crystal (Isotopes, Inc.) with a 1.6-cm transverse hole through which the effluent was carried in an 8-mm quartz tube wound with iron resistance wire and heated. The crystal, which is very sensitive to thermal shock, was protected by a silvered air condenser placed between the heated counting tube and the crystal wall. With this configuration, the effluent tube could safely be heated to 160°.

The output of the photomultiplier was connected to a Hewlett-Packard Model 5201 L scaler-timer pulse height analyzer, which permitted the continuous recording of the counts accumulated in consecutive time intervals. The analyzer was set to accept pulses only in the region of 0.4–1.2 MeV, in order to include the 0.511-MeV annihilation radiation and the 1.022-MeV sum peak. Other instrumental techniques were standard for this type of experimentation. Samples were monitored as previously described.[13]

The separation columns are listed in Table I. Most products were verified on two or more columns although a few higher boiling products were identified on one column only. Most of the identifications seemed reasonable in light of the expected chemistry.

Table I. Chromatographic Columns Used for Product Separations and Verification of Product Identity[a]

1. 18-ft, 30% Carbowax 20M (F&M Scientific) on Chromosorb WAW DMCS, 45–60 mesh (F&M Scientific)
2. 18- and 30-ft 30% Tripropionin (K&K Laboratories) on Chromosorb P, 45–60 mesh (F&M Scientific)
3. 30-ft, 35% 2-ethylhexyl acetate (Eastman Organic) on Chromosorb P, 45–60 mesh (F&M Scientific)
4. 20-ft, 30% Triisovalerin (K&K Laboratories) on Chromosorb WAW DMCS, 45–60 mesh (F&M Scientific)
5. 20-ft, 30% Dibutoxytetraglycol (Carbide and Carbon Chemicals) on Chromosorb WAW DMCS, 45–60 Mesh (F&M Scientific)
6. 14-ft molecular sieve, Linde Type 5A (Matheson Coleman and Bell), 40–60 mesh
7. 20-ft 20% Tricaprylin (K&K Laboratories) on Anakrom PA, 50–60 mesh (Analabs)

[a] All columns were fabricated from 8-mm Pyrex tubing.

Dosimetry. The integrated dose rate at the probe position in the electron synchrotron was redetermined for this work and related to the dose monitor.

The induced activity in the sample (corrected for duration of bombardment, decay, and carbon atom density) was found to be directly proportional to the integrated dose as measured by cobalt glass dosimetry.[14] The cobalt glass dosimeters were calibrated using a Fricke dosimeter at the Iowa State University cobalt-60 source.

The contribution to the measured sample activity from interfering nuclear reactions [$^{16}O(\gamma,n)^{15}O$, $^{16}O(\gamma,t)^{13}N$, and $^{16}O(\gamma,\alpha n)^{11}C$] as a result of oxygen in the sample and bulblet was determined to be less than 6% of the total sample activity under the least favorable experimental conditions (short bombardment periods and low carbon atom density, *e.g.*, methanol which has equal numbers of oxygen and carbon atoms). This determination is based on the production ratios of ^{15}O, ^{13}N, and ^{11}C from ^{16}O relative to ^{11}C from ^{12}C by computer resolution of the decay curves of several synchroton irradiated compounds.

In a typical irradiation the integrated dose rate was determined to be about 5×10^{19} eV/(g min), but the instantaneous dose rate is considerably higher. The electron synchrotron is a pulsed machine with a cycle time of 1.7×10^{-2} sec and a pulse duration time of 4×10^{-8} sec. The carbon-11 is produced only during the pulse and as a consequence finds itself in a radiation field considerably more intense than would be indicated by the integrated dose and dose rate values.

In studying the dependence of yields on concentrations of radiation produced radicals, a wide variation in dose rate would be desirable. With the synchrotron it was not possible to obtain such a variation, and the total dose was varied by changing the irradiation time. Thus irradiation times ranged from 2 to 20 min; the variation in dose rate was roughly twofold in different irradiations but was kept to ±20% during any single run. Examination of the data for dose rate dependence over this range did not show any trends with statistical significance.

Absolute Yield Calibration. In order to place the measurements on the absolute basis of fraction of the total ^{11}C found in each compound, samples of isopentane were irradiated and monitored in the standard procedure, placed in a sample breaker, heated above the boiling point, and broken. The vapor was carried in an air

---

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

(11) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath & Co., Boston, Mass., 1957, p 289.

(12) P. Arthur, W. M. Haynes, and L. P. Uarga, *Anal. Chem.*, **38**, 1630 (1966).

(13) D. E. Clark and A. F. Voigt, *J. Am. Chem. Soc.*, **87**, 5558 (1965).

(14) N. J. Kreidl and G. E. Blair, *Nucleonics*, **14** (3), 82 (1956); 17 (10), 58 (1959); G. F. Blair, *J. Am. Ceram. Soc.*, **43**, 426 (1960).

stream into a CuO oxidation furnace at 750°, and the resulting carbon dioxide was passed through a 500-cm^3 expansion chamber and a 16-ft column packed with Chromosorb P. It was found necessary to use the expansion chamber and column in order to avoid a sudden surge of gas through the counting system. The activity in the broad CO_2 peak was recorded in 30-sec intervals and the flow rate was measured. These measurements were used for a computer calculation of the total activity using the basic relationship

$$\text{yield }\% = \frac{(C - b)(e^{\lambda t_p})R}{Me^{\lambda t_m}F} \tag{1}$$

in which C = total counts observed under elution peak, b = background counts under peak, t_p = time after bombardment to measurement of peak, t_m = time after bombardment to monitor count, M = monitor count (counts/min), R = flow rate, F = calibration factor relating flow and monitor counters, and λ = decay constant of ^{11}C. For this purpose the yield was assumed to be 100% and the product $(C - b)e^{\lambda t_p}$ was replaced by the sum of n such terms for the n separately measured intervals. From six determinations the value 2.775 ± 0.007 was obtained for F.

The combustion process was tested for completion by oxidizing several weighed samples of inactive *n*-octane (Phillips, Research Grade) and collecting the carbon dioxide on ascarite. Complete recovery was obtained.

Results and Discussion

In interpreting recoil carbon data, the effect of the accompanying radiation field on the product distribution must be considered. Radiolysis of the target material produces radicals and molecules which may be reactive toward the initial recoil ^{11}C atoms or toward radical intermediates which they form during thermalization. The effects of changes in dose and dose rate and of radical scavengers have been used in assessing the significance of radiolysis. In liquid systems iodine and DPPH are commonly used scavengers. At low concentrations the scavenger does not interfere with the hot reaction processes but may remove the recoil atom if it is in the form of thermal radical intermediates. The scavenger also reduces the concentration of radiation produced radicals which are not labeled and thereby changes the course of reaction for the recoil species.

In this investigation the yields of all observable products from methanol and ethanol were determined as a function of dose in both unscavenged and I_2-scavenged systems. For methanol a limited amount of data was also obtained in DPPH-scavenged systems.

Recoil Chemistry of Atomic Carbon in Methanol. Radiation Chemistry of Methanol. Knowledge of the radiation chemistry of methanol is of prime importance to an understanding of the reactions involved in these studies. A brief review of this intensively studied subject may be helpful. The primary ions produced in the electron bombardment of methanol vapor and their abundances[15] are CH_2OH^+ (100), CH_3OH^+ (68), CHO^+ (52), CH_3^+ (23), and CO^+ (15). In the liquid the solvent cage effect would tend to increase the yields of the first two at the expense of the others by reducing the loss of H_2 and $\cdot OH$.[16]

These ions react with the solvent to produce the $CH_3OH_2^+$ ion and various products, particularly HCHO, $\cdot CH_2OH$, and CO.[16] The $CH_3OH_2^+$ ion can be neutralized by reaction with solvated electrons producing hydrogen atoms, and $CH_3O\cdot$ and $CH_3\cdot$ radicals.[10] These radicals in turn react with the solvent to produce the hydroxymethyl radical, $\cdot CH_2OH$. The unstable species in largest instantaneous concentration in the unscavenged system are $\cdot CH_2OH$, $\cdot H$, $CH_3OH_2^+$, and e^-(solv).

In the iodine-scavenged system the reaction sequence is modified by reactions of iodine with both radicals and electrons.[17] In the body of the liquid the I_2 is more than competitive with $CH_3OH_2^+$ for the solvated electrons as a result of its much higher concentration (10^{-3} *M*) and the very high rate constant for the reaction.[18] Within radiation spurs this may not be the case.

The reactions of the primary ions with the solvent should be similar to the unscavenged systems since most of these reactions occur rapidly within the spur. The following changes are expected in the over-all reaction sequences.[17]

$$I_2 + e^-(\text{solv}) \longrightarrow [I_2^-] \xrightarrow{I_2} I_3^- + I\cdot^{19} \tag{2}$$

$$CH_3OH_2^+ + I_3^- \longrightarrow CH_3OH + HI + I_2 \tag{3}$$

$$H\cdot + I_2 \longrightarrow HI + I\cdot \tag{4}$$

$$CH_3\cdot + I_2 \longrightarrow CH_3I + I\cdot \tag{5}$$

$$\cdot OH + I_2 \longrightarrow HIO + I\cdot \tag{6}$$

$$\cdot CH_2OH + I_2 \longrightarrow ICH_2OH + I\cdot \tag{7}$$

$$2I\cdot \longrightarrow I_2 \qquad (8$$

The iodine atoms and HI may also react directly with the radicals. The iodohydrin from (7) is unstable and reacts with the solvent. The net result of the addition of iodine is the reduction in concentrations of the radicals and ions present in the unscavenged system. Iodine also reacts with thermal radicals containing ^{11}C to alter the reaction paths of the labeled fragments. Little information is available on the effect of DPPH on methanol radiolysis.

Recoil Carbon Chemistry in Methanol. From Table II it may be seen that recoil ^{11}C atoms stabilize in a variety of products and that the yields of some of these are dose dependent. The product spectrum can be explained on the basis of primary reactions involving insertion of ^{11}C, ^{11}CH, or $^{11}CH_2$ into C–H or O–H bonds or interactions of ^{11}C with a lone pair on oxygen.

No evidence was found for the insertion of any of these radicals or of their primary products into the C–O bond. This is in agreement with published studies[6] on the reaction of recoil ^{14}C with methanol followed by degradation of the ethanol product which showed 95.1% of the ^{14}C in the methyl group. Attempts to observe the insertion of methylene and other carbenes into C–O bonds have also been unsuccessful.[20]

The primary products of insertion reactions either fragment or react as radical intermediates with solvent molecules, radiation-produced radicals, or added scavengers. Many reaction paths were considered but discarded because of inconsistencies. Those which agreed with these results and those of other studies are presented in outline form in Figures 1–3. It will be

---

(15) L. Friedman, A. Long, and M. Wolfsberg, *J. Chem. Phys.*, 27, 613 (1957).

(16) P. Wilmenius and E. Lindholm, *Arkiv Fysik*, **21**, 97 (1962).

(17) G. Meshitsuka and M. Burton, *Radiation Res.*, **8**, 285 (1958).

(18) A rate constant of 5.1×10^{10} M^{-1} sec^{-1} for the reaction of I_2 with a hydrated electron has been determined by J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, **68**, 1524 (1964). The value for the solvated electron in methanol should not be significantly different.

(19) The decomposition of the transient species $[I_2^-]$ is speculative and is based on the observation of the reaction $2I_3^- \rightarrow I_3^- + I^-$ by L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, **61**, 1089 (1957).

(20) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 36.

Table II. Yields of Radioactive Products in the $^{12}C(\gamma,n)^{11}C$ Reaction in Methanol

	Yields, % of total ^{11}C			
	Unscavenged^a		X_{I_2} = 1.01 × $10^{-3\,a}$	
Product	a	b	a	b
Carbon monoxide	15.6 ± 1.9	9.5 ± 1.6	24.2 ± 0.3	24.9 ± 0.3
Carbon dioxide	...	...	0.21 ± 0.03	0.13 ± 0.03
Methane	3.97 ± 0.2	3.97 ± 0.2	2.47 ± 0.09	2.66 ± 0.09
Ethane	0.91 ± 0.15	1.07 ± 0.15	0.60 ± 0.11	0.80 ± 0.11
Ethylene	9.84 ± 0.4	9.89 ± 0.4	8.44 ± 0.3	9.01 ± 0.3
Acetylene	14.9 ± 0.6	13.8 ± 0.9	15.4 ± 0.7	16.1 ± 0.7
Propylene	0.41 ± 0.03	0.27 ± 0.03	0.41 ± 0.05	0.25 ± 0.05
Dimethyl ether	4.64 ± 0.14	4.51 ± 0.2	4.08 ± 0.2	4.12 ± 0.2
Methyl ethyl ether	0.45 ± 0.03	0.50 ± 0.03	0.37 ± 0.07	0.41 ± 0.07
Methyl vinyl ether	0.39 ± 0.04	0.30 ± 0.04	0.42 ± 0.3	0.47 ± 0.3
Dimethoxymethane	4.53 ± 0.2	4.08 ± 0.2	9.5 ± 0.4	10.6 ± 0.2
1,1-Dimethoxyethane	...	...	3.54 ± 0.8	2.53 ± 0.8
Acetaldehyde	~3.9	0.85 ± 0.2	...	t
Methyl formate	t	t	0.65 ± 0.09	0.60 ± 0.09
Methyl acetate	3.57 ± 0.13	3.05 ± 0.13	...	...
Ethanol	8.29 ± 0.6	8.88 ± 0.6	4.97 ± 0.3	5.66 ± 0.3
1-Propanol	1.47 ± 0.2	1.78 ± 0.2	0.39 ± 0.09	0.33 ± 0.09
Allyl alcohol	1.87 ± 0.2	1.76 ± 0.2	1.05 ± 0.13	1.21 ± 0.13
2-Methoxyethanol	3.68 ± 0.4	3.28 ± 0.4	0.99 ± 0.13	1.33 ± 0.13
Ethanediol	0.95 ± 0.2	1.11 ± 0.2	...	...
1,2-Propanediol	5.73 ± 0.5	8.50 ± 1.7	...	...
1,3-Propanediol	1.14 ± 0.4	1.32 ± 0.4	...	...
Methyl iodide	...	...	3.38 ± 0.2	3.72 ± 0.2
Vinyl iodide	...	...	2.10 ± 0.09	2.67 ± 0.09
Unknown	...	...	~9.3	~5.3
	86.2	78.4	92.5	92.8

[a] Dose (eV/molecule): a, 0.009; b, 0.036. t = trace observed.

noted that if I_2 is present, it reacts in place of the $\cdot H$ and $\cdot CH_2OH$ radicals by reactions 4 and 7 which remove these radicals and by competition with them as a result of its higher concentration.

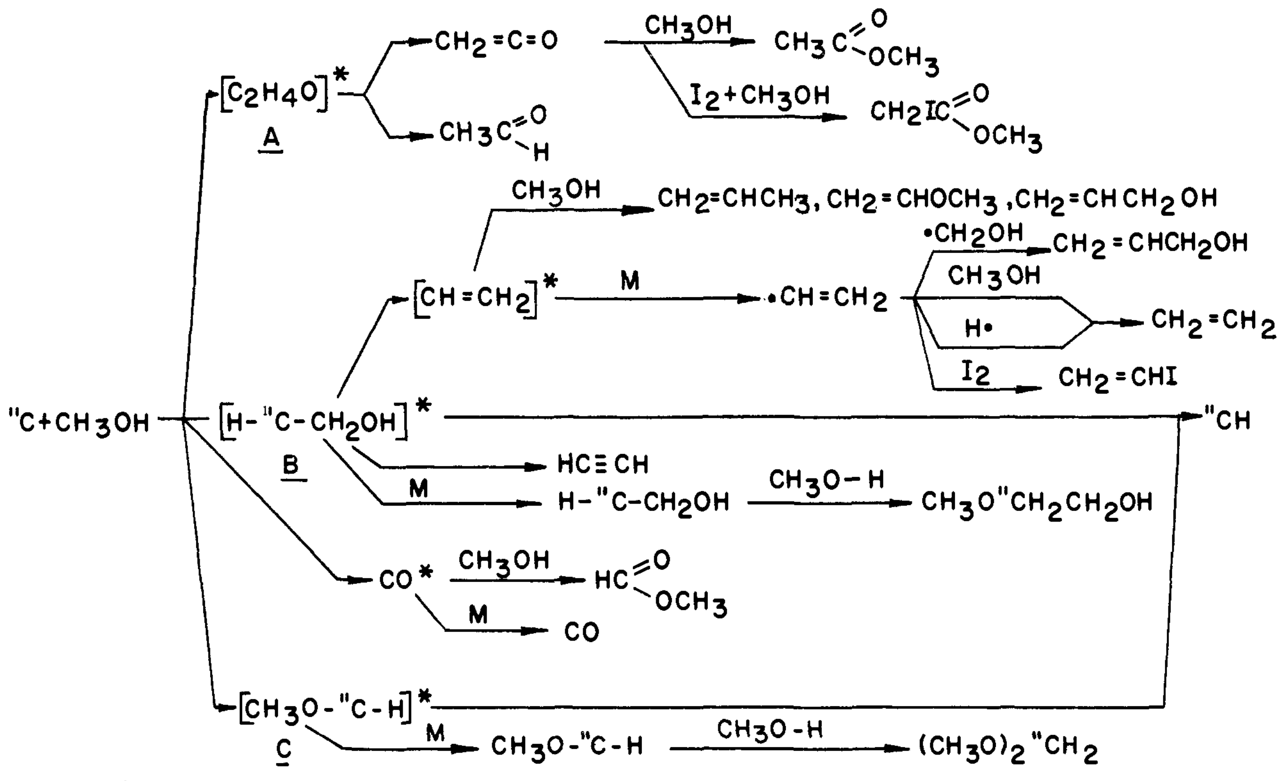


Figure 1. Chemistry of recoil carbon in methanol, reactions of ^{11}C.

Carbon Atom Reactions. The initial insertion of the recoil ^{11}C atom into the C–H and O–H bonds of methanol produces excited adducts (carbenes) B and C, Figure 1. The adducts may fragment, rearrange, or collisionally deactivate and react with the solvent.

Yields of the products of reactions with the solvent indicate a preference for O–H bond insertion. Two successive insertion reactions lead to the three

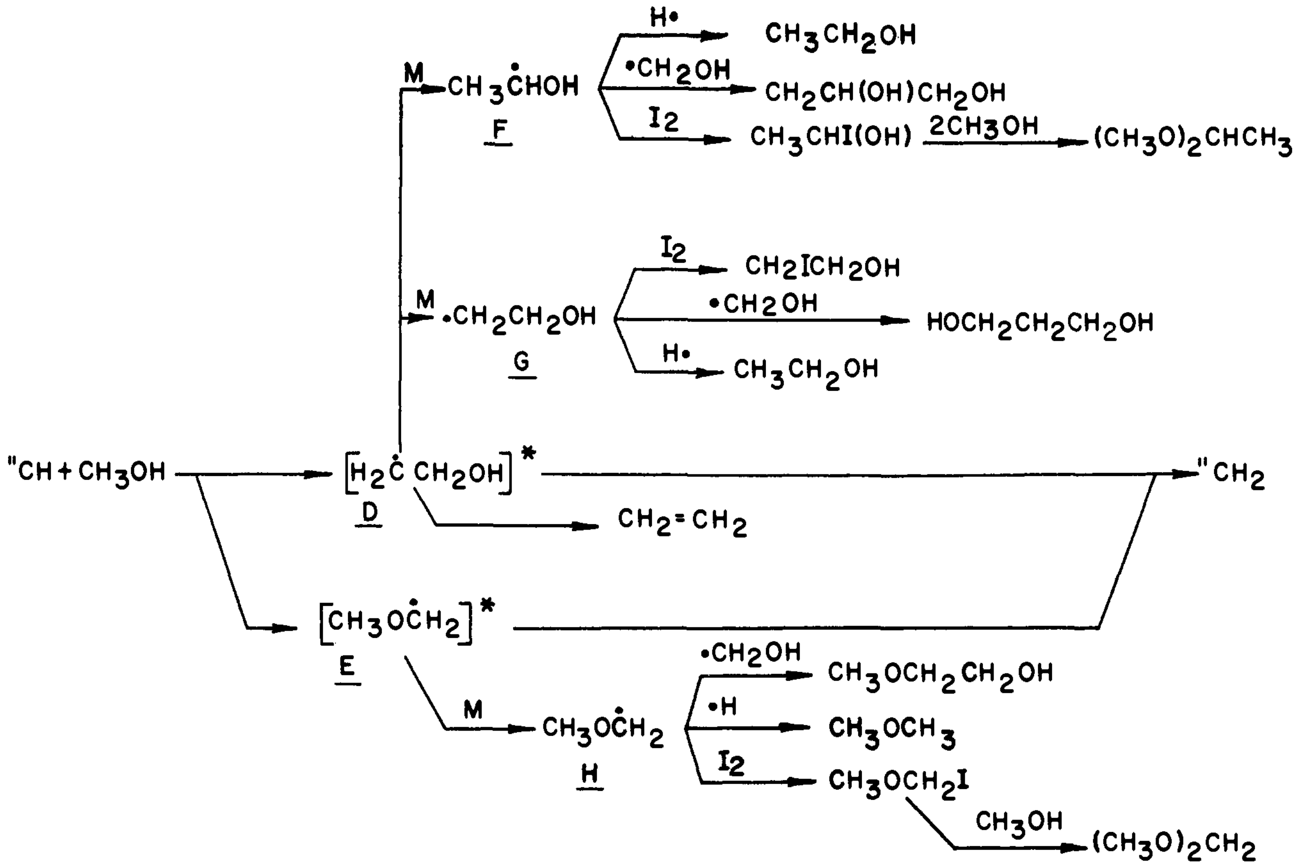


Figure 2. Chemistry of recoil carbon in methanol, reactions of ^{11}CH.

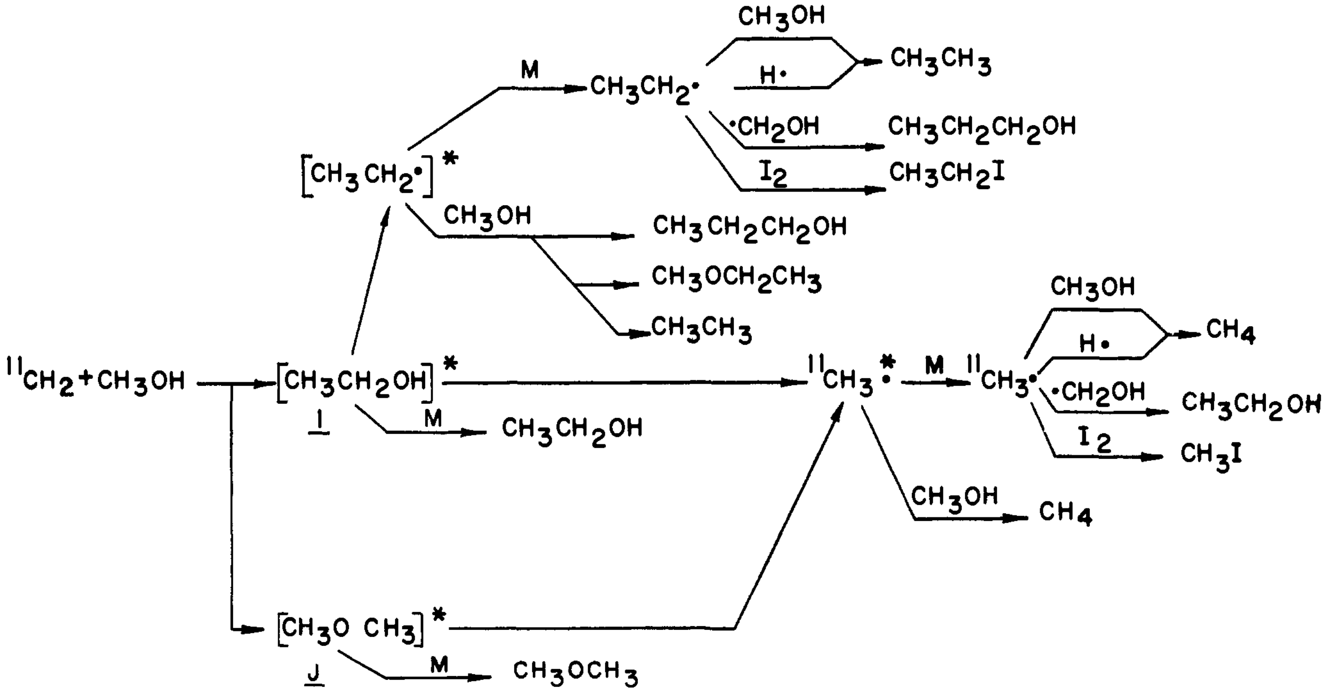


Figure 3. Chemistry of recoil carbon in methanol, reactions of ^{11}CH$_2$ and ^{11}CH$_3$.

compounds $(CH_3O)_2{}^{11}CH_2$ by two O–H insertions, $CH_2OH{}^{11}CH_2CH_2OH$ by two C–H insertions, and $CH_3O{}^{11}CH_2CH_2OH$ by O–H and C–H insertions in either order. As shown in Table II, the dimethoxymethane yield is enhanced by I_2; the double-insertion mechanism is logical for part of its yield. The 1,3-propanediol yield is completely removed by I_2 indicating radical mechanism only for its production; thus the hydroxymethylcarbene does not insert in the C–H bond. The 2-methoxyethanol yield is greatly reduced by I_2, indicating that much of it is formed by a radical reaction (see Figure 2). The nonradical portion of the yield is probably formed by the reaction sequence of Figure 1, C–H followed by O–H insertion rather than the reverse order. Other evidence for the preference for O–H insertion comes from the reaction of dimethoxycarbene with methanol which yields trimethoxymethane, but no product corresponding to C–H insertion.[21]

Excited adduct A is written to cover any kind of intermediate which cannot be characterized as resulting from bond insertion. The formation of acetaldehyde and products for which ketene is a precursor may be more readily explained through such an intermediate than through B, but B could rearrange to give acetaldehyde or ketene. Methyl acetate and acetaldehyde are both shown as having A as a precursor, but there is no real evidence for this. An intermediate similar to A was proposed by Cacace, *et al.*, in the formation of acetonitrile-^{11}C from methylamine.[4]

Excited intermediates B and C may fragment to ^{11}CH, and B may fragment to acetylene or an excited vinyl radical. Within experimental error, the acetylene-^{11}C yield is independent of dose and scavenger as expected if it is formed by a rapid unimolecular decomposition.

The excited vinyl radical (or another entity with similar formula and excitation) appears to undergo rapid radical–molecule reactions with the solvent to form propylene, methyl vinyl ether, or allyl alcohol. For the first two this postulate is supported by the scavenger independence of their yields. The collisionally deactivated vinyl radical can react with radiation-produced radicals or it can abstract hydrogen from methanol. Since the ethylene-^{11}C yield is not scavenger dependent, the abstraction and hydrogen radical reactions are not major mechanisms for its production (see below).

In the iodine-scavenged system, the vinyl radical reacts preferentially with iodine to form vinyl iodide. The addition of scavenger substantially reduces the yield of allyl alcohol; the yield of vinyl iodide-^{11}C (+2.1%) is balanced by the reduction for ethylene-^{11}C (−1.4%) and allyl alcohol-^{11}C (−0.8%).

The mechanism for production of ^{11}CO is of considerable interest. From its yield in other oxygen-containing compounds,[22] it appears to be formed by interaction of the ^{11}C atom with a lone pair of electrons on an oxygen atom rather than a bonding pair between oxygen and its neighbors. In the unscavenged system, the yield of ^{11}CO is highly dose dependent, as are those of acetaldehyde and 1,2-propanediol. These products and ^{11}CO$_2$ appear to be related, probably through the solvated electron as a common reactant.[23]

In published investigations[24] on the reactions of hydrated electrons with CO and CO$_2$ in dilute methanol solution, glycolaldehyde and glycolic acid, respectively, were observed as products. The mechanism postulated involved the formation of $\cdot CO^-$ and $\cdot CO_2^-$ by reactions with the hydrated electron followed by neutralization to CHO and $\cdot CHO_2$ by hydrogen ions and reaction of these radicals with radiation produced $\cdot CH_2OH$ radicals to give the products. The order of the last two reactions may be reversed, but present indications are that the neutralization occurs first.

The two products, $CH_2OH^{11}CHO$ and CH_2OH-$^{11}CO_2H$, were not observable in our experiments, but indirect evidence points to this type of mechanism. The ^{11}CO yield is reduced at higher dose as a result of the removal of CO by the solvated electrons. The absolute amount of a compound present is expected to increase with time of irradiation. However, the "yield" as defined here is the ratio of ^{11}C in a product to the total ^{11}C. If the product interacts with a radiation produced reactant, this ratio may decrease with increasing irradiation time. In the presence of iodine, which effectively removes the solved electrons, the ^{11}CO yield is greatly increased and shows no dose dependence, and a small yield of ^{11}CO$_2$ is observed.

The yield of acetaldehyde, which is only seen in the unscavenged system, is also highly dose dependent. The reduction in its yield on going from low to high dose (−3.0%) is balanced by the increase for 1,2-propanediol (+2.8%). It is postulated that these yields are related by the reaction sequence

$$CH_3CHO + e^-(solv) \longrightarrow CH_3CHO^-$$

$$CH_3CHO^- + CH_3OH_2^+ \longrightarrow CH_3\dot{C}HOH + CH_3OH$$

$$CH_3\dot{C}HOH + \dot{C}H_2OH \longrightarrow CH_3CHOHCH_2OH$$

Additional support for this proposal comes from an experiment in which carrier quantities of acetaldehyde were added to the methanol sample before irradiation for the purpose of protecting the acetaldehyde-^{11}C from reduction. This resulted in an increase in the yield of acetaldehyde of >5.7% and a decrease in 1,2-propanediol of 6.0%. The addition of iodine to methanol reduced the yields of these two compounds to zero, as the result of an interference which must have occurred in an earlier part of the reaction sequence. An unidentified product appeared with a yield (9.3%) nearly the same as the reduction in yield of acetaldehyde and 1,2-propanediol (−9.6%).

Other reaction pathways are suggested for the production of 1,2-propanediol as shown by the reaction of $CH_3\dot{C}HOH$, intermediate E in Figure 2, with CH_2OH. Iodine reduces the concentration of $\cdot CH_2OH$, replacing it to form the intermediate $CH_3CHI(OH)$. Under conditions of acid catalysis,[25,26] *gem*-halohydrins react with alcohols to form acetals

$$CH_3CHI(OH) + CH_3OH \longrightarrow CH_3CHIOCH_3 + H_2O$$
$$CH_3CHIOCH_3 + CH_3OH \longrightarrow CH_3CH(OCH_3)_2 + HI$$

or the iodine may be replaced first to give the hemiacetal

$$CH_3CHI(OH) + CH_3OH \longrightarrow CH_3CH(OH)OCH_3 + HI$$

Since the usual conditions for these reactions, acid or higher temperatures, are not obviously present during the irradiations, a reaction sequence such as this may not appear likely. However, it accounts very nicely for the observed appearance of dimethoxyethane and disappearance of 1,2-propanediol and is suggested in spite of these difficulties. Dimethoxyethane is also observed in the DPPH-scavenged system and a similar mechanism can be postulated.

---

(21) R. W. Hoffman and H. Haeuser, *Tetrahedron Lett.*, 197 (1964).

(22) G. F. Palino, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1967.

(23) The rate constants for the reactions of hydrated electrons with CO, CO$_2$, and CH$_3$CHO have been reported as 10^9, 7.7×10^9, and 5.4×10^9 M^{-1} sec^{-1}: E. J. Hart, J. K. Thomas, and S. Gordon, *Radiation Res. Suppl.*, 4, 74 (1964); *J. Phys. Chem.*, **68**, 1271 (1964). The constants for the solvated electrons in methanol are probably not significantly different.

(24) (a) J. Holian, G. Scholes, and J. J. Weiss, *Nature*, **191**, 1386 (1961); (b) G. Scholes, M. Simic, and J. J. Weiss, *ibid.*, **188**, 1019 (1960).

(25) D. J. Cram and G. S. Hammond, "Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 293.

(26) L. Simmons, *Chem. Rev.*, **55**, 301 (1955).

Table III. Scavenger Dependence of the C_1 and C_2 Product Yields in Methanol[a]

	Product				
Scavenger, mole fraction	CO	CH_4	C_2H_6	C_2H_4	C_2H_2
0.00	15.0 ± 1.9	3.97 ± 0.2	0.92 ± 0.15	9.85 ± 0.4	14.9 ± 0.6
I_2 (1.01×10^{-3})	24.2 ± 0.3	2.48 ± 0.09	0.61 ± 0.11	8.46 ± 0.3	15.4 ± 0.7
I_2 (2.26×10^{-3})	23.6 ± 0.8	2.08 ± 0.17	0.50 ± 0.06	7.23 ± 0.2	14.5 ± 0.4
DPPH (satd)	25.4 ± 0.5	3.02 ± 0.2	0.90 ± 0.05	9.66 ± 0.4	16.1 ± 0.4

[a] Dose 0.010 eV/molecule.

In the DPPH-scavenged system, labeled acetaldehyde and methyl acetate are observed in yields similar to those in the unscavenged system, a fact consistent with the hypothesis of a nonradical precursor for these products. Ketene-^{11}C will not react with DPPH, but in the iodine-scavenged system the reaction to form methyl iodoacetate may be expected to occur (see Figure 1). Since the yields of acetylene and carbon monoxide are higher in the DPPH-scavenged system (see Table III), DPPH appears to be an efficient scavenger for solvated electrons and hydrogen atoms.

Reactions of Methyne Radical. The chemistry of this intermediate has been virtually unknown until recent years.[27,28] In the carbon recoil system, methyne can be formed by either the "insertion–decomposition" mechanism (from B or C of Figure 1) or by hydrogen abstraction. The CH radical is considered to exhibit insertion properties similar to those of the carbon atom and has been singled out as the major precursor to the ethylene-^{11}C observed in saturated hydrocarbon systems.[13,27]

In methanol, insertion of ^{11}CH into the C–H or O–H bond is expected to give D and E, Figure 2. Fragmentation reactions yielding methylene radicals and ethylene are well known from experiments on hydrocarbons. Deexcitation of D may produce two types of ethanol-^{11}C radicals, the more stable having the α-hydrogen removed. Neither of these is able to abstract hydrogen from methanol, and they stabilize by the radical–radical reactions shown. The reaction of G with the $\cdot CH_2OH$ radical is the major mechanism for the production of 1,3-propanediol. The production of iodoethanol-^{11}C in the iodine-scavenged system could not be verified; various attempts to elute it were unsuccessful, possibly a result of its thermal instability.[29]

The $CH_3OCH_2\cdot$ radical, H in Figure 2, is unable to abstract hydrogen from the solvent and forms stable products by radical–radical reactions. The scavenged part of the 2-methoxyethanol-^{11}C is believed to be formed in this manner. Iodine scavenges the $CH_3OCH_2\cdot$ radical forming CH_3OCH_2I, an α-halo ether which is expected to act with methanol[26] to form $CH_2(OCH_3)_2$. This appears logical as the major reason for the increased yield of dimethoxymethane-^{11}C in the iodine-scavenged system. A similar increase was not observed in the DPPH-scavenged system; CH_3OCH_2–DPPH may be less reactive than CH_3OCH_2I toward methanol.

The small yield of ethanediol-^{11}C in the unscavenged system and its removal by iodine suggests a mechanism such as

$$^{11}\dot{C}H_2OH + \dot{C}H_2OH \longrightarrow {}^{11}CH_2OHCH_2OH$$

although the formation of $^{11}\dot{C}H_2OH$ is not understood. Iodine would interfere with this reaction by combining with either of these radicals.

Reactions of the Methylene Radical. Insertion reactions of methylene are well known. Intermediates I and J, Figure 3, can fragment or deactivate to stable ethanol and dimethyl ether. Methyl ethyl ether probably results from the reaction of an excited ethyl-^{11}C radical with the solvent since its yield is independent of scavenger. That part of the yields of 1-propanol and ethane which is unscavenged probably results from similar reactions.

The thermal ethyl-^{11}C radical may pick up or abstract hydrogen to form ethane, or it may react with $\cdot CH_2OH$ to form 1-propanol. The participation of a C_2 entity in the reaction to form 1-propanol was suggested by Oae, *et al.*, as a result of degradative studies on the 1-propanol-^{14}C produced during reactor irradiations of a methanol–ammonia solution.[6] These experiments showed that 98% of the activity was nearly equally distributed between the 2 and 3 positions. The authors' suggestion that labeled ethylene is the reactive intermediate appears very reasonable.

The failure to detect ethyl iodide as a product is puzzling at first since it would be expected to replace ethane and propanol in the scavenged system. This discrepancy can be explained if the reaction

$$CH_2{=}CH_2 + \cdot H \longrightarrow CH_3\dot{C}H_2$$

which would be blocked by iodine, is the principal mode of formation of ethyl radicals rather than the decomposition of I, Figure 3. The reduction of the yields of ethane and propanol on addition of iodine would thus be due to interruption of their production mechanisms before rather than after the formation of ethyl radicals.

On the basis of the yields of ethanol (4.97%) and dimethyl ether (4.08%), it appears that the single O–H bond in methanol is more reactive toward methylene than the individual C–H bonds are. On a per-bond basis the ratio of probabilities for insertion–stabilization in O–H/C–H bonds is 2.4. This indicates that the O–H bond in methanol is more reactive than the C–H bond and that its insertion adduct stabilizes more readily or both. Higher reactivity of the O–H bond toward carbene insertion was discussed earlier.[30]

Reactions of Methyl Radicals. As seen in Figure 3, in the unscavenged system the methyl radical can abstract hydrogen from the solvent or react with radiation

---

(27) G. Stoecklin and A. P. Wolf, *J. Am. Chem. Soc.*, **85**, 229 (1963).

(28) (a) W. Braun, J. R. McNesby, and A. M. Bass, *J. Chem. Phys.*, **46**, 2071 (1967); (b) D. R. Safrany, R. R. Reeves, and P. Harteck, *J. Am. Chem. Soc.*, 86, 3160 (1964).

(29) C. L. McCabe and J. C. Warner, *ibid.*, 70, 4031 (1948).

(30) The relative activities for the insertion of singlet methylene into O–H as compared to the primary C–H bond in methanol and ethanol have been measured to be 21.8 and 21.2, respectively: J. A. Kerr, B. V. O'Grady, and A. F. Trotman-Dickerson, *J. Chem. Soc., A*, 897 (1967). The decreased selectivity observed in the recoil carbon system may be the result of the higher internal or kinetic energy of the recoil methylene.

Table IV. Yields of Radioactive Products as a Result of the $^{12}C(\gamma,n)^{11}C$ Reaction in Ethanol

	Yields, % of total ^{11}C			
	Unscavenged[a]		$X_{I_2} = 9.7 \times 10^{-3}$ [a]	
Product	a	b	a	b
Carbon monoxide	14.5 ± 0.4	14.6 ± 0.4	16.9 ± 0.6	17.6 ± 0.6
Methane	4.25 ± 0.2	4.38 ± 0.2	2.74 ± 0.08	2.61 ± 0.08
Ethane	1.04 ± 0.08	0.91 ± 0.08	0.57 ± 0.03	0.81 ± 0.03
Ethylene	7.76 ± 0.4	6.27 ± 0.4	7.18 ± 0.12	7.40 ± 0.12
Acetylene	12.8 ± 0.4	10.6 ± 0.4	13.8 ± 0.3	13.7 ± 0.3
Propane	0.40 ± 0.05	0.38 ± 0.05	0.26 ± 0.01	0.24 ± 0.01
Propylene	3.84 ± 0.15	3.55 ± 0.15	3.48 ± 0.10	3.54 ± 0.10
Allene	0.80 ± 0.10	0.70 ± 0.10	0.72 ± 0.10	0.46 ± 0.10
Propyne	2.82 ± 0.16	2.75 ± 0.16	2.99 ± 0.14	2.84 ± 0.14
Methyl ethyl ether	2.86 ± 0.15	2.84 ± 0.15	2.50 ± 0.18	2.77 ± 0.18
Methyl vinyl ether	0.39 ± 0.05	0.33 ± 0.05	~0.3	
Diethyl ether	0.51 ± 0.10	0.43 ± 0.10	0.33 ± 0.08	0.28 ± 0.08
Diethoxymethane	2.04 ± 0.17	2.07 ± 0.17	6.67 ± 0.5	7.26 ± 0.5
1,1-Diethoxyethane and/or ethyl propionate	...	...	1.70 ± 0.8	4.92 ± 0.4
Acetaldehyde	2.48 ± 0.4	2.50 ± 0.4	...	0.52 ± 0.2
Propionaldehyde	1.23 ± 0.4	1.11 ± 0.4	...	t
Ethyl formate	t	t	1.34 ± 0.3	0.75 ± 0.3
Ethyl acetate	1.89 ± 0.10	1.77 ± 0.10	...	0.8
Acetone	2.39 ± 0.3	2.63 ± 0.3	2.87 ± 0.2	3.06 ± 0.2
2-Propanol	5.76 ± 0.2	5.08 ± 0.2	3.01 ± 0.17	3.02 ± 0.17
1-Propanol	4.54 ± 0.08	5.01 ± 0.08	4.01 ± 0.09	3.76 ± 0.09
Allyl alcohol	5.0 ± 0.3	3.5 ± 0.3	4.41 ± 0.40	3.93 ± 0.40
2-Propyn-1-ol	1.25 ± 0.2	0.91 ± 0.2	1.22 ± 0.04	1.28 ± 0.04
1-Butanol	0.95 ± 0.13	0.86 ± 0.13	0.48 ± 0.05	0.39 ± 0.05
2-Butanol	1.88 ± 1.0	2.22 ± 1.0	0.53 ± 0.16	0.60 ± 0.16
1-Buten-3-ol	2.33 ± 0.4	2.56 ± 0.4	0.60 ± 0.04	0.58 ± 0.04
1-Pentanol	0.64 ± 0.08	0.47 ± 0.08	t	t
3-Ethoxy-1-propanol	0.75 ± 0.14	0.51 ± 0.14	...	...
Methyl iodide	...	...	3.29 ± 0.2	3.41 ± 0.2
Diiodomethane	...	...	~0.7	
Total	85.1	78.9	82.6	87.2

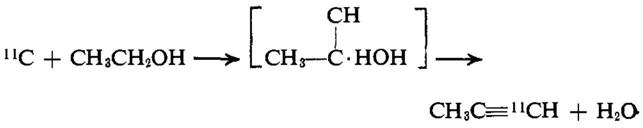
[a] Dose (eV/molecule): a, 0.010; b, 0.050. t = trace observed.

produced radicals. The addition of I_2 scavenger reduces the yields of both ethanol-^{11}C (−3.3%) and methane-^{11}C (−1.5%) consistent with the proposed reaction scheme. However, the $^{11}CH_3I$ yield (+3.4%) is not sufficient to account for these yield reductions, and other mechanisms, such as those with F and G, Figure 2, may play a part.

Recoil Carbon Chemistry in Ethanol. The carbon atom recoiling in ethanol stabilizes in an even larger variety of compounds than in methanol, and more of these products remain unidentified (Table IV). The radiolysis of ethanol is similar to that of methanol[31]; the $CH_3\dot{C}HOH$ and ·H radicals are dominant, and their concentrations are reduced by iodine. In pure ethanol the ^{11}CO and acetaldehyde-^{11}C yields are not dose dependent. Radiation produces a rather high concentration of acetaldehyde (G = 3.14), and it is expected to act as an efficient electron scavenger.[32]

The yields of a number of the unsaturated products, particularly ethylene and acetylene, are reduced as the dose is increased, probably as a result of reductions by radiolytically produced hydrogen atoms, solvated electrons, or radicals.

Reasonable reaction mechanisms can be proposed for most of the other products from ethanol, in many cases quite analogous to those for methanol. The propynol and propyne yields are independent of scavenger and nearly independent of dose; *i.e.*, they are hot products. The probable mechanism is the insertion of ^{11}C into a β or α C–H bond and the loss of H_2 or H_2O. Thus for propyne



$$^{11}C + CH_3CH_2OH \longrightarrow \left[CH_3-\overset{CH}{\overset{|}{C}}\cdot HOH\right] \longrightarrow CH_3C\equiv{}^{11}CH + H_2O$$

The intermediate in this reaction could readily rearrange to the enol form of acetone, and the excited propyne could isomerize to allene.

Products in the ethanol system analogous to those observed in methanol are expected to have similar mechanistic pathways, but yields may be lower because of the increased possibilities for reaction of the ^{11}C. Diethoxymethane-^{11}C, though probably formed by the double-insertion mechanism proposed in Figure 1 for dimethoxymethane, is found in substantially lower yield. The products 2-butanol and 1-buten-3-ol are homologs of 1-propanol and allyl alcohol in the methanol system. A major fraction of both is believed to result from the reactions of labeled C_2 entities with radiation produced $CH_3\dot{C}HOH$ radicals.

Repeating the comparison of the reactivities of the O–H and C–H bonds to methylene on the basis of the yields of methyl ethyl ether and the propanols, it is found that on a per-bond basis, $O\text{–}H/C\text{–}H_{(prim)}$ = 1.87, and $O\text{–}H/C\text{–}H_{(sec)}$ = 1.67. Although these are lower than the ratio found in methanol, the hypothesis of greater reactivity of the O–H bond is supported.

---

(31) J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 349.
(32) E. Hayon and J. J. Weiss, *J. Chem. Soc.*, 3962 (1961).

Acknowledgments. The authors are very grateful to the members of the Iowa State University electron synchrotron staff, especially Dr. Alfred Bureau and Mr. James Sayre.

Triplet–Triplet Energy Transfer from the Second Triplet State of Anthracene. Spectroscopic Methods[1]

R. S. H. Liu and R. E. Kellogg

Contribution No. 1496 from the Central Research Department,
Experimental Station, E. I. du Pont de Nemours and Company,
Wilmington, Delaware. Received August 28, 1968

Abstract: Selective excitation of anthracene in mixed crystals (host, dibenzofuran or biphenyl) containing guest molecules of anthracene and naphthalene-d_8 at $-195°$ produces naphthalene phosphorescence. This result is interpreted as energy transfer from T_2 of anthracene to the host triplet, followed by exciton diffusion to naphthalene traps. Escape efficiency of triplet excitation from anthracene to naphthalene-d_8 traps in dibenzofuran is $(1.1 \pm 0.3) \times 10^{-4}$.

The second triplet states, T_2, of anthracene[2] and several substituted anthracenes[3] have been shown to lie energetically below the lowest excited singlet states, S_1. In these cases, intersystem crossing from S_1 populates the T_2 state first.[2,3] The lifetimes of these higher triplet states are apparently sufficiently long, as demonstrated in several chemical studies,[4] that they can act as donors in triplet–triplet energy-transfer processes in solution with reasonable efficiency. For 9,10-dibromoanthracene, the T_2 lifetime was shown from Stern–Volmer plots to be $(2.2 \pm 0.5) \times 10^{-10}$ sec.[4a]

$$D_{T_2} + A_{S_0} \longrightarrow D_{S_0} + A_{T_1}$$

While some transfer pairs in solution diffuse apart without "reverse" quenching,[5] the slow radiative rate of the triplet acceptor makes spectroscopic detection difficult because of "reverse" quenching by later collisions, *i.e.*

$$D_{S_0} + A_{T_1} \longrightarrow D_{T_1} + A_{S_0}$$

We report here a study of energy transfer from anthracene T_2 in mixed crystals where the excitation transfers to the host crystal, migrates to a remote trap, and ultimately emits.

Results and Discussion

The donor–acceptor pair chosen for this study is anthracene and naphthalene-d_8 with either biphenyl (BP) or dibenzofuran (DBF) as host. The important energy levels for these compounds are shown schematically in Figure 1.[6,7]

The mixed crystals were prepared between quartz plates separated by lead spacers. The spectrophotometer used to record emission spectra has been described.[3] A collimated beam from a PEK 100-W high-pressure mercury lamp was used as the excitation source. The 3660-Å line was isolated with a *f*/3.5 Bausch & Lomb monochromator, combined with a Corning 7-54 filter. A Corning 3-74 filter was placed at the entrance slit. Samples of purified biphenyl and dibenzofuran were generously provided by Dr. G. J. Sloan.

Excitation with 3660-Å light of 0.1-mm mixed crystals containing 0.1% (by weight) anthracene and 1% naphthalene-d_8 at 77°K showed weak naphthalene phosphorescence (in addition to anthracene fluorescence (Figure 2)). The intensity in dibenzofuran (DBF) was five times that in biphenyl (BP).

In view of the relative energy levels of these compounds, the logical pathway to produce naphthalene phosphorescence is (1) $S_0 \rightarrow S_1$ excitation of anthracene followed by intersystem crossing to T_2; (2) energy transfer to the host T_1 and exciton migration away; (3) trapping by naphthalene-d_8 T_1 and subsequent phosphorescence.

Control samples containing only naphthalene-d_8 showed the phosphorescence down by a factor of 20 in DBF and by a factor of 10 in BP, showing that direct absorption by the naphthalene is not responsible. In DBF, the control phosphorescence appeared to be due to residual anthracene impurity in DBF or naphthalene or both. Doping with 9,10-diphenylanthracene[8] (Φ_f = 1.00 ± 0.05)[9] in lieu of anthracene shows a weaker phosphorescence than the control due to competition for excitation with the anthracene impurity and less efficient intersystem crossing indicating that the donor state is in

---

(1) The Role of Second Triplet States in Solution Photochemistry. V.

(2) R. E. Kellogg, *J. Chem. Phys.*, **44**, 411 (1966).

(3) R. G. Bennett and P. J. McCartin, *ibid.*, **44**, 1969 (1966).

(4) (a) R. S. H. Liu and J. R. Edman, *J. Am. Chem. Soc.*, in press; and also previous papers of this series; (b) R. S. H. Liu and J. R. Edman, *ibid.*, **90**, 213 (1968); (c) R. S. H. Liu and D. M. Gale, *ibid.*, **90**, 1897 (1968); (d) N. C. Yang, N. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Letters*, 3657 (1964); (e) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Am. Chem. Soc.*, **90**, 1957 (1968); (f) P. de Mayo, J. P. Pete, and M. Tchir, *ibid.*, **89**, 5712 (1967). The last three report chemical reactions involving higher triplet states.

(5) Such a "reverse" transfer has been identified in one case: R. S. H. Liu, *ibid.*, **90**, 1899 (1968).

(6) Naphthalene T_2 is not included in the diagram because the state is too high in energy (30,800 cm^{-1})[7] to be involved in this study.

(7) D. M. Hanson and G. W. Robinson, *J. Chem. Phys.*, **43**, 4175 (1965).

(8) We acknowledge Dr. R. G. Beunnett for first suggesting this experiment to us.

(9) E. C. Lim, J. D. Laposa, and J. M. H. Yu, *J. Mol. Spectry.*, **19**, 412 (1966); see also, I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 130.