Molecular Geometry and Bond Energy. III. Cyclooctatetraene and Related Compounds

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Abstract: The LCAO–MO–SCF–PPP ($\pi + \sigma$) method, developed in parts I and II[1] of this series, for conjugated hydrocarbons, has been applied to eight-membered ring compounds. The variations in the predicted bond lengths of these compounds are discussed; the neutral rings are compared with the dianions and dications. The stabilization energy per CC bond (SECC), derived from the calculated π and σ bond energies, suggests that any composite ring unit that can accommodate approximately "$4n + 2$" π electrons will greatly stabilize the molecule in which it occurs.

The chemistry of cyclooctatetraene (COT) has been experimentally[2,3] and theoretically[4] investigated previously. However, (i) the exact nature of the strain energy of a planar COT ring, (ii) the bond lengths in the COT dianion, and other related neutral molecules or charged ions, (iii) the π-electron density distribution, (iv) the stabilities of the molecules resulting from π delocalization and σ compression, and (v) their relative susceptibilities to reduction and oxidation still require a more thorough analysis. Many new compounds related to COT have been recently synthesized and many unsuccessful attempted syntheses reported. The present theory attempts to correlate calculated molecular properties with the established experimental properties, while predictions of the properties of other molecules yet to be synthesized, together with the systematic trends in their general chemical properties, have been made.

Theory

Within the π-LCAO–MO–SCF method,[1a] the total π-electronic energy, E_π, can be partitioned into "atomic" and "binding" energies; thus the atomic energy

$$E_\pi = \sum_i^{\text{all C atoms}} q_i W_\pi + \sum_i \frac{1}{4} q_i^2 \gamma_{ii} + \sum_{i<j}\left[(q_i - 1)(q_j - 1) - \frac{1}{2}P_{ij}^2\right]\gamma_{ij} + \sum_{i<j} 2P_{ij}\beta_{ij} \quad (1)$$

where q_i is the self-consistent π-electron density of the ith π AO, and P_{ij} is the π-bond order. The "atomic" energy is a sum of valence-state ionization potentials, W_π, of the π electrons on a trigonally hybridized carbon σ core. On the conventional energy scale, W_π is negative. The "binding" energy includes π-electrostatic interactions, expressed in terms of the one-center and two-center electronic repulsion energies, γ_{ii} and γ_{ij} (positive quantities), and a negative resonance energy, β_{ij}, which describes the additional stabilization of the π electrons on bond formation. Hence, E_π is also negative. All these parameters, W_π, γ_{ii}, γ_{ij}, and β_{ij}, are evaluated semiempirically. W_π is -11.16 eV and γ_{ii} is 11.134 eV,[1a] taken from Hinze and Jaffé's valence-state energies. γ_{ij} ($\equiv 14.398/\sqrt{R_{ij}^2 + (14.398/\gamma_{ii})^2}$ eV) is expressed[1a] in terms of Ohno's semiempirical form. β_{ij} is a third degree polynomial function[1a] of interatomic distance R_{ij}. They have been carefully analyzed in part I.[1a]

For a neutral or a positively charged, closed-shell conjugated hydrocarbon, the total π-bond energy, $E_{\pi\text{b}}$, of the molecule is defined as

$$E_{\pi\text{b}} = -\left[E_\pi - \sum_i q_i W_\pi\right] \quad (2)$$

Note that $E_{\pi\text{b}}$ is positive, unlike the negative "binding" energy in eq 1: the π-*bond* energy and the π-*binding* energy must be clearly distinguished at all times.

In an anion, the "atomic" energy is $[\Sigma_i q_i W_\pi + \gamma_{ii}]$, because one of the π AO's has two π electrons in it, and the energy of this $\ddot{\text{C}}^-$ unit[5] is equal to $[2W_\pi + \gamma_{ii}]$, instead of $2W_\pi$. Hence, $E_{\pi\text{b}}$ for an anion (or dianion) is

$$E_{\pi\text{b}} = -\left[E_\pi - \sum_i q_i W_\pi - n_l \gamma_{ii}\right] \quad (3)$$

where n_l is the number of lone-pair π electrons in an AO; n_l equals 1 for an anion, 2 for a dianion, etc.

The total CC σ bond energy, $E_{\sigma\text{b}}$, is evaluated as a sum of all individual CC bond energies, each of which is a function of its specific bond length, R_{ij}. The bond lengths are calculated by a direct maximization of $E_{\pi\text{b}}$ and $E_{\sigma\text{b}}$ with respect to each R_{ij}. The SECC can be readily derived[1a] by taking the difference between the calculated $E_{\pi\text{b}} + E_{\sigma\text{b}}$ of the real molecule and the energy of the most stable hypothetical valence-bond reference structure, and then dividing the difference in energy by the total number of CC bonds in the molecule. This SECC is a good measure of the stability of these compounds and permits comparisons between them and their anions and cations.

Results and Discussion

The bond energies, $E_{\pi\text{b}}$ and $E_{\sigma\text{b}}$, together with the stabilization energies, SECC, are tabulated in Table I; the bond lengths are given in Table II, corresponding to the molecular geometries in Figure 1. The heat of atomization, ΔH_a (25°), for a "neutral" conjugated

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Table I. Bond Energies and Stabilization Energies (in Electron Volts)

Molecule		$E_{\pi b}$	$E_{\sigma b}$	SECC
$I_a{}^0$	C_8H_8	10.458	28.870	0.1568
$I_a{}^{2-}$	C_8H_8	8.100	29.882	0.2018
II^0	$C_{10}H_{10}$	13.636	35.874	0.1936
III^0	$C_{14}H_{12}$	17.101	55.517	0.1402
III^{2+}	$C_{14}H_{12}$	18.488	55.663	0.3551
IV^-	$C_{13}H_{11}$	19.500	51.670	0.4470
V^0	$C_{16}H_{12}$	23.329	66.197	0.3102
V^{2-}	$C_{16}H_{12}$	22.490	67.074	0.4063
VI^0	$C_{18}H_{14}$	25.603	72.861	0.2503
VII^0	$C_{18}H_{14}$	25.533	72.991	0.2533
$VIII^0$	$C_{22}H_{18}$	30.489	87.242	0.2185
$VIII^{2+}$	$C_{22}H_{18}$	33.096	88.406	0.4460

Table II. Bond Lengths (in Å)

Molecule	*a*	*b*	*c*	*d*	*e*	*f*
$I_a{}^0$	1.354	1.461				
ϵ^a	1.340	1.476				
$I_a{}^{2-}$	1.416					
II^0	1.350	1.463	1.348	1.469	1.472	1.346
III^0	1.416	1.394	1.416	1.402	1.492	
III^{2+}	1.378	1.443	1.387	1.427	1.439	
IV^-	1.448	1.369	1.442	1.382	1.483	1.426
	g 1.395	*h* 1.410				
V^0	1.347	1.469	1.412	1.401	1.403	1.398
V^{2-}	1.413	1.415	1.453	1.420	1.391	1.428
VI^0	1.347	1.469	1.346	1.472	1.409	1.403
VII^0	1.469	1.347	1.468	1.353	1.480	1.463
	a' 1.351	b' 1.464	c' 1.404	d' 1.413	e' 1.391	f' 1.410
$VIII^0$	1.463	1.350	1.464	1.464	1.350	1.367
	a' 1.463	b' 1.353	c' 1.459	d' 1.354		
$VIII^{2+}$	1.352	1.465	1.362	1.476	1.343	1.453
	a' 1.416	b' 1.396	c' 1.417	d' 1.397		

[a] Electron diffraction data, ref 6a.

hydrocarbon is the sum $[E_{\pi b} + E_{\sigma b} + n_{CH}E_{CH}]^{1a}$ where n_{CH} is the number of CH bonds, each with a bond energy of E_{CH} (102.13 kcal/mole).

COT (I). In view of the chemical and physical properties of COT, it has long been classified as nonaromatic. The experimental and theoretical bond lengths (in Å) of COT and the related 1,3-butadiene are compared in order to demonstrate the effect of π-electron delocalization on the geometries of these nonaromatic polyene molecules (see Table III).

Table III

Exptl electron diffraction data	*trans*-1,3-Butadiene (planar)	COT (tub)
A-1 (1957)[6b]	*s* 1.483	D_{2h} 1.462
	d 1.337	1.334
A-2 (1966)[6a]	*s* 1.467	D_{2d} 1.476
	d 1.344	1.340
Theoretical	(planar)[1b]	(planar)
B (this work)	*s* 1.470	1.461
	d 1.338	1.354

COT has a nonplanar tub conformation (D_{2d}) with alternating *s*ingle (1.476 Å) and *d*ouble (1.340 Å) bond lengths.[6a] The bond length, *d*, in COT is, however, still longer than that of ethylene (1.334 Å),[1b] being a perfectly isolated double bond.

Two points can be made. Firstly, the recent set of experimental bond lengths, A-2,[6a] confirms the qualitative idea that the decrease in the double-bond length *d* and the increase in the single bond length *s* in going from the planar 1,3-butadiene[7] to the nonplanar COT are a result of decreased conjugation in the nonplanar COT molecule. This conclusion does not follow from the earlier set of electron-diffraction data, A-1.[6b]

Secondly, the theoretical bond length's pattern, B, of single-bond contraction and double-bond elongation in going from the planar 1,3-butadiene to the planar strain-free COT suggests an increased conjugation effect in the planar molecule.

Consequently, it is possible to measure the bond-length changes in COT when it goes from planar to tub; the single and double bonds are changed by + and −0.015 Å, respectively.

There is a substantial decrease in both $E_{\pi b}$ and $E_{\sigma b}$ to compensate for the minimization of the strain energy of the planar ring: ΔH_a estimated for a planar strain-free COT is 1723.6 kcal/mole compared to the experimental value[9] of 1714.6 kcal/mole for the tub molecule. This difference of 9 kcal/mole is hence a lower bound value for the COT ring-strain energy, since minimization of strain is achieved only at the expense of a loss in $E_{\pi b}$ and $E_{\sigma b}$.

Estimates of the potential barrier for the conversion of the *planar-strained* to the tub COT have been experimentally obtained from several COT derivatives,[3,10] and theoretically obtained by consideration of the total electronic energies of different conformations.[4] From these an upper bound value for the COT ring *strain energy* has been estimated to be 25 kcal/mole.[3,4,10]

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(6) (a) M. Tratteberg, *Acta Chem. Scand.*, **20**, 1724 (1966); (b) O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).

(7) The new A-2 experimental single-bond length of 1,3-butadiene, 1.476 Å, rules out the possibility of this being a pure single sp^2 carbon–carbon bond length; this possibility was previously suggested by Dewar,[8] in the light of the earlier experimental result A-1 of 1.483 Å for this bond. The alternations of bond lengths in 1,3,5-hexatriene have been determined experimentally (M. Tratteberg, *Acta Chem. Scand.*, 22, 628 (1968)) and are in agreement with those estimated for this molecule in ref 1b.

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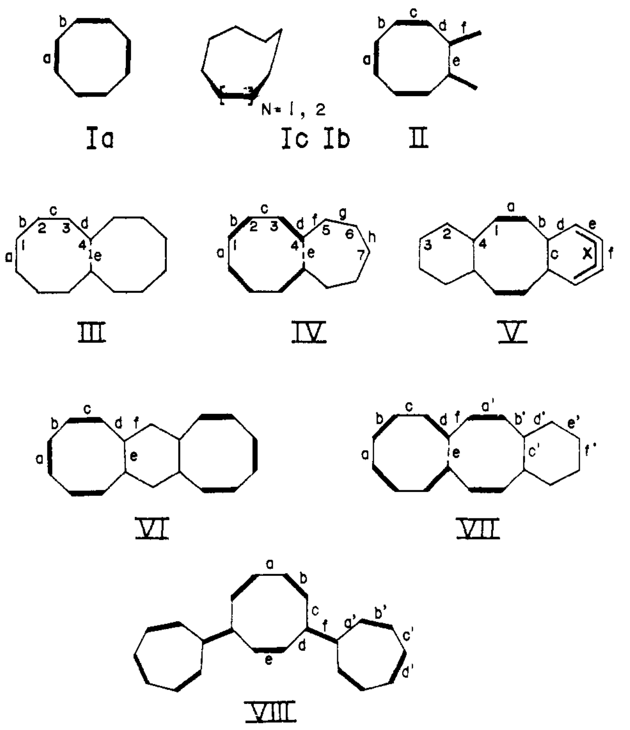

Figure 1. Bond-length diagrams. Geometries corresponding to bond lengths of 1.35 ± 0.02 Å (—); 1.42 ± 0.05 Å (—); and 1.47 ± 0.02 Å (- - - -).

The experimental olefinic properties of COT clearly demonstrate the absence of conjugation between the nearly orthogonal double bonds in the tub form. Chlorination[11] of COT gives an unusual *cis*-addition product in both the *endo, cis* and *exo, cis* boat forms. The theoretically predicted geometry of COT consists of four double bonds, in agreement with the olefinic properties above.

COT is easily reduced by alkali metals to form a planar radical anion[2] and, by further reduction, a planar dianion.[12] The dianion is stabilized relative to its neutral precursor by the presence of 10 π electrons, as predicted by Hückel's "$4n + 2$" rule.[8] The SECC of COT, 0.1586 eV, and of its dianion, 0.2108 eV, are consistent with their relative experimental order of stability. An additional factor in the stability of the COT dianion, I^{2-}, lies in the equality of the bond lengths in the ring at 1.416 Å. Coulson[13] calculated 1.409 Å for this bond length by means of a bond-length *vs.* bond-order relationship. This bond length is indeed longer than the bond length of benzene, 1.397 Å.[1a]

The equivalence of the eight ring protons in the COT radical anion is reflected in its esr spectrum. Their equivalence in the COT dianion ring is shown by the nmr spectrum; the absorptions occur at low field. These properties imply that the Jahn–Teller distortions[2] are unimportant, and that the π electrons in these anions are delocalized over the eight-carbon skeleton of the COT ring.

Hückel's $4n + 2$ rule[8] for the stability of a molecule was initially derived from the MO properties of monocyclic polyenes, whose bonding (and nonbonding) MO's can be fully occupied by $4n + 2$ π electrons. However, in the fused ring compounds related to the monocyclic polyenes, the ability of the π electrons to retain a $4n + 2$ number on a composite planar ring skeleton is also important, as demonstrated by many experimental properties described below.

Thus COT has a high proton affinity, because the cation formed by protonation of COT is a monohomotropylium cation, I_c^+, with six π electrons delocalized on a seven-carbon planar skeleton;[14] the monohomo COT dianion,[12] I_b^{2-}, is a homoaromatic ten π-electron system, and consequently possesses properties analogous to those of the COT dianion, I_a^{2-}, while in the complex $[(COT)Mo(CO)_3]$[15a] only six π electrons on a six-carbon planar skeleton in COT participate as a ligand in coordination with the central metal molybdenum, as shown by nmr. The X-ray molecular structure of $[(CH_3)_4(COT)Cr(CO)_3]$[15b] shows the same six sp^2-carbon planar skeleton in COT, acting as a ligand, as in the molybdenum complex. The validity of the $4n + 2$ rule in similar composite ring systems is analyzed in the following molecules.

7,8-Dimethylenecyclooctatetraene (II). II is a higher vinylog of *o*-xylene; it is an unstable yellow oil that polymerized readily on standing. Its uv spectrum[16] is very similar to that of COT. The bond lengths in the eight-membered ring of II are approximately the same as those in COT (Table II). Since the two exocyclic double bonds, *f* (1.346 Å), are joined by a single bond, *e* (1.472 Å), in this molecule, their reactivity with dienophiles is promoted and tetrahydro COT derivatives are formed.[16] The SECC is 0.1936 eV in II, compared to 0.1586 eV in COT (I). The higher SECC in II than in I is consistent with the fact that the SECC of a linear polyene has been shown to increase with increasing chain length.[1b]

Octalene (III). Octalene (III) has 14 π electrons. If the central cross-linkage does not significantly destabilize the peripheral [14]annulene in III, octalene is expected to be "aromatic." However, recent attempts[17] to synthesize III have been unsuccessful, and dehydrogenation of dihydrooctalene[18] under vigorous conditions did not give octalene. However, hexabenzooctalene has been synthesized,[19] but it is nonaromatic and nonplanar since its uv spectrum is similar to that of COT.

The calculated bond lengths for a planar molecule of III reveal a very long cross-linkage, *e*, equal to 1.492 Å. Bond *e* is elongated, so that the molecule can achieve the stability of a [14]annulene moiety, but since the SECC of III is 0.1402 eV, it is obvious that *e* is a strong destabilizing perturbation on the system. The SECC of III is even lower than that of COT. Hence, III cannot

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be planar, since the stabilization of the planar molecule by π delocalization and σ compression cannot overcome the significant strain energy of *two* eight-membered rings. In parallel, a recent theoretical analysis[20] shows that the most stable conformation for octalene is two tub-like COT fused together with assumed strong bond alternations.

However, the octalene dication III^{2+} has a substantially larger $E_{\pi b}$ and $E_{\sigma b}$, relative to III, and the bond lengths of III^{2+} show a larger variation from 1.38 to 1.44 Å. Note that in this dication, carbon 3 bears a net "negative" charge of -0.016, while carbons 1, 2, and 4 have net positive charges of 0.1275, 0.2888, and 0.1992.

Although the cyclooctatetraenecycloheptatrienyl anion (IV$^-$) is isoelectronic with octalene III, the SECC of 0.4470 eV for IV$^-$ is much higher than the 0.1402 eV of III. This can be explained in terms of the total net charge of the COT ring in IV$^-$, which absorbs an extra 0.5446 electron into its π network. This stabilizes the molecular ion. In IV$^-$, a substantial net negative charge of 0.2168 electron is located at carbon 3; the bond lengths in the COT unit are alternating, with bond *e* (1.483 Å) the longest. The seven-membered ring has bond lengths close to the benzenoidal distance (1.4 Å).

The acidity of a hydrocarbon could be reflected by the stability of its anion. Cyclooctatetraenecycloheptatriene (IV) exchanges with potassium *t*-butoxide to give the anion IV$^-$, while cycloheptatriene (T) exchanges to give the corresponding tropylium anion (T$^-$). The SECC is 0.4470 eV for IV$^-$ and 0.5151 eV for T$^-$, which accounts for the experimental observation that the exchange is 20 times slower for IV than for T.[18]

***sym*-Dibenzocyclooctatetraene (V).** The stabilization is increased in V by the fusion of two benzo groups to the COT ring, with a substantial increase of SECC to 0.3102 eV in V from 0.1586 eV in COT. The fusion of a benzo group to any bond in COT will fix this bond length at around 1.4 Å. Bond *c* in V equals 1.412 Å compared to 1.354 Å in COT (I). The two double bonds *a* in V react like a diolefin.

V is readily reducible to the corresponding anion radical and dianion by alkali metals or by polarographic reduction,[21] which indicates significant interaction between the benzene rings and the central COT. In the dianion, charges are delocalized over the three rings, with the COT unit, presumably planar, having an induced ring current.[21] This delocalization is illustrated by the net charges calculated for the COT unit (-1.022), and for the four-carbon skeleton (-0.489) "X" (Figure 1) in the composite benzene ring. The higher SECC of V^{2-} relative to V can be attributed to the extra electrons accommodated by the COT ring. The COT bond lengths in V^{2-} (a = 1.413 Å and b = 1.415 Å) are very similar to the bond length of 1.416 Å in COT dianion I^{2-}. Since V^{2-} consists of $4n + 2$ electrons, the central cross-linkage *c* is long, 1.453 Å. This behavior is like that of the cross-linkage *e* in octalene (III).

By correlating the proton chemical shifts (corrected for ring-current effects) in the nmr spectrum of V^{2-} with the benzene protons and the COT dianion protons, net charges have been evaluated "experimentally"[21] as C(1) -0.19, C(2) -0.06, and C(3) $-$ 0.16. The predicted net π charges are C(1) -0.1939, C(2) -0.0525, C(3) -0.1919, and C(4) -0.0616. The agreement is satisfactory and is a useful check on the validity of the predicted π-charge densities.

Dicyclooctatetraeno[1,2-4,5]benzene (VI) and Benzooctalene (VII). By analogy with [18]annulene, both VI and VII might be aromatic, but all experimental data[18,22] is against their possessing aromatic character. The peripheral COT ring bond lengths in VI are alternating single and double, while the central benzene ring bond lengths are approximately 1.4 Å.

Catalytic hydrogenation of VI leaves an unsaturated benzene ring but saturated peripheral COT ring bonds.[22] This agrees with the predicted geometry of VI. The benzene bond length *e* (1.409 Å) in VI and *c* (1.404 Å) in VII are consistent with the general conclusion drawn in V, of the effect on the bond lengths in the COT ring due to the fusion with a benzo group. In addition, the cross-linkage *e* (1.480 Å) in VII is pseudo-single, similar to bond *e* in its parent octalene (III).

5,8-Bis(cycloheptatrienylidene)cyclooctatriene-1,3,6 (VIII). A recent attempt to synthesize VIII[23] led to a reductive dimerization of the tropylium ion by the COT dianion. When the $4n + 2$ rule is applied to the seven- and eight-membered rings, a polar structure in the ground state for VIII would stabilize the molecule. However, the calculation predicts a total net charge migration of less than 0.1 electron from the tropylium ring to the COT ring, and the low SECC (0.2185 eV) for VIII suggests a fairly unstable molecule. The dication VIII^{2+} is, however, stable; its SECC is 0.4460 eV. This is due to the total net charge of $+0.8856$ localized in the tropylium ring and of $+0.2288$ in the COT ring. The geometries of VIII and VIII^{2+} are drastically different. Bond lengths in the tropylium ring of the dication are all close to 1.4 Å, compared to large alternations in the bond lengths of its neutral precursor. Bridge bond f is double in VIII, but only single in VIII^{2+}. This illustrates the presence of two isolated pseudo-tropylium cations in the dication VIII^{2+}.

The calculation carried out for the VIII^{2-} dianion leads to divergence. There are large charge fluctuations between the two seven-membered rings in VIII^{2-}, while the central COT unit maintains a fairly constant total π density of 8.7 electrons, as shown in Table IV which follows.

Table IV. Total π-Electron Densities of VIII^{2-}

SCF iterations	1st tropylium ring	Central COT	2nd tropylium ring
1	7.60	8.80	7.56
2	7.53	8.84	7.65
3	7.77	8.78	7.45
4	7.25	8.76	8.00
5	8.40	8.74	6.86
6	6.54	8.66	8.80
etc.			

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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]

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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

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(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.

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