Table II. Comparative Electron Spin Resonance Parameters for α-Magnesioalkyl Radicals and Alkyl Radicals

Radical	Temp, °C	$\langle g \rangle$	a_α^H, G	a_β^H, G	ρ_α
$CH_3\dot{C}HMgCH_2CH_3$	−99	2.00293	18.24	24.35	0.83
$CH_3\dot{C}H_2$	−99	2.00278	22.28	27.00	0.92
$CH_3\dot{C}HCH_3$	−99	2.00273	21.97	24.68	0.84
$CH_3\dot{C}HOCH_2CH_3$	−47	2.00330	13.93	21.72	0.74

that IV is present in relatively high concentrations.[7] The steady-state concentration of IV relative to III depends on the organomagnesium compound and is generally higher from RMgCl than from R_2Mg and in diethyl ether compared to tetrahydrofuran. Part of the difference is related to the variation in the degree of association of organomagnesium compounds with structure and the solvent.[8] It is especially noteworthy that CH_3CH_2MgF, which is *strongly* dimeric in solution,[9] affords only IV and no III.

The hydrogen splitting in the magnesiomethyl radical II is significantly smaller than that in the methyl radical I. Spin withdrawal from carbon by the magnesium atom is probably similar to that of the lithiomethyl radical described earlier.[10] An estimate of the spin density (ρ_α) on the α carbon can be obtained from the Fessenden–Fischer relationship[11] in eq 3 for the series

$$a_{CH_3} = Q^{CH_3}\rho_\alpha = 29.30\rho_\alpha \tag{3}$$

of radicals in Table II. Furthermore, the small difference in the g factors between IV and III is associated with the rather small spin–orbit coupling constant for magnesium.[12]

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(7) (a) Strictly speaking, its importance in the reaction will depend on its lifetime relative to that of alkyl radicals. (b) It should be noted that *tert*-butoxy radicals are efficient in hydrogen abstraction reactions. (c) Furthermore, the spectra of III and IV appear under conditions in which the spectra of the radicals derived from the solvent (diethyl ether or THF) were not observed (*e.g.*, see Figures 1 and 2), despite the favorable reactivities of ethers as hydrogen donors. Well-resolved spectra of α-oxyalkyl radicals were readily obtained under the same conditions in the absence of organomagnesium compounds (J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Pub.*, No. **24**, 147 (1970).

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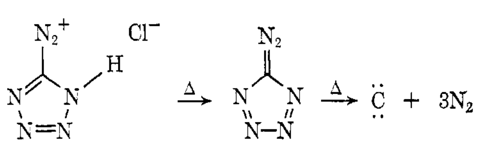
The Reaction of Chemically Generated Carbon Atoms with Carbon Monoxide

Sir:

We recently reported the formation of atomic carbon in the thermal decomposition of 5-tetrazoyldiazonium chloride (**1**).[1] The reactions of atomic carbon have been studied by such methods as generation of carbon atoms by nuclear reaction[2] and production of the atoms in a carbon arc;[3] the thermolysis reported here offers an alternative pathway for the production of carbon atoms. We wish to report additional reactions which provide further evidence for the formation of carbon atoms in the decomposition of **1**.



1

The reactions of carbon atoms are conveniently studied by coating **1** on the walls of a flask and thermally (120°) decomposing it in the presence of a gaseous reactant. When **1** is allowed to decompose in an atmosphere of carbon monoxide, a major product is carbon suboxide (**2**). The most plausible pathway for the formation of carbon suboxide is initial reaction of atomic carbon with carbon monoxide to give C_2O. The C_2O subsequently reacts with an additional molecule of carbon monoxide to generate carbon suboxide (eq 1).

$$C + CO \longrightarrow :C{=}C{=}O \qquad \Delta H = -62\ \text{kcal}$$
$$:C{=}C{=}O + CO \longrightarrow O{=}C{=}C{=}C{=}O \qquad (1)$$
$$\Delta H = -108\ \text{kcal}$$

Thermochemical considerations[4] indicate that, irrespective of the spin state of the various intermediates, both of the reactions in eq 1 are exothermic. The heats of reaction are for $C(^1D)$ reacting to produce C_2O ($^1\Sigma$) and ground-state carbon suboxide.

Nucleogenic carbon-11 atoms have been shown to react with carbon monoxide to give small yields of carbon suboxide.[5] The major product in this oxygen-scavenged system was ^{11}CO. Jacox and coworkers,[6] generating carbon atoms by photolysis of cyanogen azide in an argon matrix at 14°K, have observed a reaction with carbon monoxide to produce both C_2O and carbon suboxide. The reactive species in this study was thought to be $C(^3P)$. The vacuum-ultraviolet photolysis of carbon monoxide, in which $C(^1D)$ is produced, gives carbon suboxide as one of the products.[7] Husain and Kirsh[8] have reported flash photolysis studies of carbon suboxide in which the absorptions of both $C(^1D)$ and $C(^3P)$ are quenched by added carbon monoxide. The rate constant for the reaction of $C(^1D)$ with carbon monoxide, obtained by Husain and Kirsh, is far greater than that for $C(^3P)$ with carbon monoxide. Thus, there appears to be ample analogy for the reaction of both singlet and triplet carbon atoms with carbon monoxide to produce carbon suboxide.

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Table I. Product Yields from the Decomposition of **1** in the Presence of CO and Added Gases

Reactant(s)	N_2, mmol	Product[a] C_3O_2, mmol × 10^2	Other products,[b] mmol × 10^3
200 mm of CO	0.91 ± 0.02	1.2 ± 0.1	
200 mm of CO + 5% O_2		1.0 ± 0.1	
200 mm of CO + 10% O_2		1.2	
200 mm of CO + 20% O_2		1.1	
200 mm of CO + 100 mm of Ar		1.0	
200 mm of CO + 200 mm of Ar		1.1	
200 mm of CO + 350 mm of Ar		1.0	
200 mm of CO + 200 mm of CH_4		1.0 ± 0.1	$CH_2{=}C{=}O$, 0.23 ± 0.04; C_2H_4, 7.5 ± 0.5; C_2H_6, 0.2
200 mm of CH_4			C_2H_4, 4.7 ± 0.5
200 mm of CO + 200 mm of C_2H_4		<0.7[c]	$CH_2{=}C{=}CH_2$, 2.5; $CH_3C{\equiv}CH$, 2.0

[a] All products were identified by their ir spectra with the exception of ethane and propyne which were identified by gc retention times. [b] In all experiments HCN and C_2H_2 are produced. These products have not been included as they do not result from the reaction of carbon atoms with CO. [c] C_3O_2 was not detected by ir; a gc analysis was not performed.

In order to determine the spin state of the reacting carbon atom in our system, we have carried out the pyrolysis of **1** in the presence of carbon monoxide and various added gases. The results of these studies are given in Table I. The yield of carbon suboxide reported for the decomposition of **1** in the presence of 200 mm of carbon monoxide is an average of nine runs which have a standard deviation of 7×10^{-4} mmol. Assuming that 3 mol of nitrogen is produced per mol of carbon atom, the yield of carbon suboxide from atomic carbon is 4%. However, this is a lower limit for the yield of carbon suboxide since nitrogen may also be produced in processes which do not result in the formation of carbon atoms.

The results in Table I show that added oxygen has little effect on the yield of carbon suboxide. Since oxygen is known to be an effective scavanger of $C(^3P)$,[2,5,9] we conclude that ground-state carbon atoms are not extensively involved in the production of carbon suboxide. Triplet carbon atoms may be produced in the decomposition of **1**, but they do not react appreciably to give carbon suboxide. An attempt was made to degrade the reacting carbon atoms to their triplet ground state with increasing pressure of added argon. Table I shows that added argon has little effect on the yield of carbon suboxide. This is not surprising as flash photolysis studies[10] have shown that the rate of collisional deactivation of $C(^1D)$ to ground state by argon is small compared to the rates of reaction of $C(^1D)$.

Decomposition of **1** in an atmosphere of carbon monoxide and methane (Table I) yields ethylene as one of the products. This result is consistent with the formation of C_2O. Ethylene is known to result from the reaction of C_2O and methane.[11] Ethylene may also arise by direct reaction of carbon atoms with methane. The data in Table I show that this reaction does take place, but that the yield of ethylene is greater in the presence of a mixture of carbon monoxide and methane than in methane alone. In the reaction of carbon atoms with carbon monoxide and methane, small amounts of ketene are also produced. Possible mechanisms for the formation of ketene include (1) reaction of methylene (formed by hydrogen abstraction) with carbon monoxide or (2) hydrogen abstraction by C_2O. The formation of ketene by the reaction of methylene with carbon monoxide has been reported.[12] It is also of interest that radiolysis of carbon monoxide in the presence of methane results in the formation of ketene.[13]

The reaction of C_2O with ethylene is known to produce allene and propyne.[14] The table shows that these two substances are formed when **1** is decomposed in an atmosphere of carbon monoxide and ethylene. This result is complicated by the fact that allene and propyne are also formed by direct reaction of carbon with ethylene.[1-3] However, the yields of propyne and allene are lower when there is no carbon monoxide present. Hence, the C_2O formed appears to be trapped by ethylene.

These data provide further evidence that atomic carbon is produced in the thermal decomposition of **1**. The results of experiments carried out in the presence of oxygen indicate that products arise from the reaction of singlet carbon. A continuing problem is the low yields of products in these reactions. We are trying to circumvent this difficulty by isolation of the parent diazo compound followed by gas-phase photolysis or thermolysis.

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Reaction of Allylic Thioethers with Elemental Sulfur[1]

Sir:

Dialkyl sulfides, such as diethyl and dibenzyl sulfide, appear to be completely inert toward sulfurization with S_8 in Me_2SO-d_6, even when heated at *ca.* 80–90°

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