Chemistry of the Singlet and Triplet C_2 Molecules. Mechanism of Acetylene Formation from Reaction with Acetone and Acetaldehyde

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Abstract: C_2 reacts with acetone and acetaldehyde to produce acetylene by two distinct pathways: an intermolecular pathway which exhibits radical character and an intramolecular, nonradical pathway which involves the abstraction of two hydrogen atoms from one molecule. The intermolecular intermediate is the ethynyl radical ($HC{\equiv}C\cdot$); the intramolecular intermediate is singlet vinylidene ($CH_2{=}C{:}$). The precursors of these intermediates are postulated to be triplet and singlet C_2 molecules, respectively.

While the spectral properties of the C_2 molecule have been the subject of considerable interest,[2] little of the chemistry of this species is known. Recently it has been shown[3] that the C_2 molecule reacts with alcohols to produce acetylene by a hydrogen abstraction pathway, but no effort was made to determine the spin state(s) of the C_2 responsible for the reaction.

$$ROH + C_2 \longrightarrow C_2H_2$$

In the investigation of the chemistry of carbon vapor with oxygenated organic compounds,[4] we observed substantial quantities of acetylene. A more detailed investigation[5] of the qualitative aspects of this reaction showed that there were at least two intermediates involved in the reaction of diatomic carbon with acetone to produce acetylene. One of the pathways possessed a high degree of radical character. We suggested that the singlet ($x^1\Sigma_g^+$) ground state and long-lived triplet ($X'^3\Pi_u$) state[6] were the forms of C_2 responsible for the two pathways. This paper presents information concerning the detailed mechanism of acetylene formation from acetone and acetaldehyde.

Results and Discussion

The codeposition of carbon vapor and chlorine at a liquid nitrogen cooled surface gave tetrachloroethylene and hexachloroethane in a combined yield of 28 wt % of the carbon vaporized.[7] The possibility that these products would arise from the dimerization of dichlorocarbene or coupling of trichloromethyl radicals was not great since the dilution of the matrix, $Cl_2/C_{vap} = 600$, would make such dimerizations unlikely. A similar experiment with methanol and carbon-14 labeled carbon vapor[7] showed that ~30 wt % of the carbon vaporized appeared in products containing two carbon atoms from the arc. The methanol reaction was also run at high dilution, $CH_3OH/C_{vap} = 1000$, making coupling of C_1 fragments an unlikely route to the observed products. On this basis, vapor from a 16-V carbon arc was found to contain ~28 wt % diatomic carbon. Since the yields of acetylene were 20.6% from acetone and 24.3% from acetaldehyde, we suspected that the acetylene produced from both these substrates on codeposition with carbon vapor at a liquid nitrogen cooled surface was formed from C_2. This hypothesis was supported by thermodynamic considerations since the carbon–hydrogen bonds in acetylene are among the strongest formed by hydrogen atoms.[8]

$$\begin{array}{c} (CH_3)_2C{=}O \\ \text{or} \\ CH_3CHO \end{array} + C_2 \longrightarrow C_2H_2$$

$$C_2 + H \longrightarrow C_2H \qquad H = 132 \text{ kcal/mol}$$
$$C_2H + H \longrightarrow C_2H_2 \qquad H = 114 \text{ kcal/mol}$$

To demonstrate that the acetylene from acetone and acetaldehyde was a product of C_2 reaction rather than from a fragmentation pathway, such as those favored in "hot" atom systems,[9-11] reactions were run with ^{14}C enriched carbon vapor.[3] If C_2 is the precursor of acetylene, then the acetylene isolated from a reaction with ^{14}C carbon vapor should have a relative molar activity of 2.00 since both of its carbon atoms would be derived from the arc. If C_1 were the precursor the relative molar activity would be 1.00.

$$(CH_3)_2C{=}O + {}^{14}C \longrightarrow H^{14}C{\equiv}^{14}CH$$

The results of the ^{14}C enriched vapor reactions are presented in Table I. The carbon monoxide produced

Table I. Carbon-14 Content of Acetylene from Acetone and Acetaldehyde

Substrate	Product	Yield[a]	Relative molar[b] activity
Acetone	CO	17.3	[1.00]
	C_2H_2	20.6	2.16
Acetaldehyde	CO	13.7	[1.00]
	C_2H_2	24.3	1.92

[a] Wt % carbon vaporized in product. [b] $(\text{Curies/mole})_{\text{samp}}/\text{curies/mole})_{\text{CO}}$.

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[1] National Institutes of Health Predoctoral Fellow (1967–1970).

[2] E. Clementi and H. Clementi, *J. Chem. Phys.*, **36**, 2824 (1962), and cited references.

[3] P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, **88**, 5933 (1966).

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

[5] P. S. Skell, J. H. Plonka, and R. F. Harris, *Chem. Commun.*, 689 (1970).

[6] E. A. Ballik and D. A. Ramsay, *Astrophys. J.*, 137, 61, 84 (1963).

[7] R. F. Harris, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1968.

[8] M. Cowperthwaite and S. H. Bauer, *J. Chem. Phys.*, **36**, 1743 (1962).

[9] J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, 41, 3267 (1964).

[10] H. Ache and A. Wolf, *J. Amer. Chem. Soc.*, **88**, 888 (1966).

[11] G. F. Palino and A. F. Voight, *ibid.*, **91**, 242 (1969).

from the deoxygenation of the carbonyl compounds by atomic carbon was taken as the molar activity standard of 1.00 since it was shown to arise from only carbon atoms of the vapor[12] and there was no degradative pathway to nonactive carbon monoxide operating.

$$R_2C{=}O + {}^{14}C \longrightarrow R_2C: + {}^{14}CO$$

The ^{14}C data in Table I require that both carbon atoms in the acetylene samples are derived from the arc. Since the weight ratio of reactive substrate to carbon vaporized is quite high (600:1000), the possibility that the labeling result may be explained by a methine dimerization mechanism[13,14] appears very unlikely since it woud require a sufficiently long life for this species to permit diffusional encounter in the presence of substrate species which are probably highly reactive with CH.

$$2CH \not\longrightarrow HC{\equiv}CH$$

Earlier it was reported[5] that in the codeposition of carbon vapor with a 1:1 mixture of acetone and perdeuterioacetone the acetylene produced was labeled in a manner that required two pathways for its production, one intramolecular to produce C_2D_2 and C_2H_2, the other intermolecular and random in the manner in which it acquired hydrogen atoms (see below for details). Further, the intermolecular component of the reaction was selectively side tracked by good H-atom donors such as toluene or acetaldehyde. The ability of these substances to effectively scavenge the intermolecular intermediates when present in a matrix which was predominately acetone led us to postulate triplet C_2 and ethynyl radical, $\cdot C_2H$, as the mobile and selective intermediates of the intermolecular reaction; singlet C_2 was assigned to the intramolecular path.

$$\upharpoonleft\downharpoonright C{=}C \upharpoonleft\downharpoonright \xrightarrow{RH_2} H_2C{=}C \upharpoonleft\downharpoonright \xrightarrow{\sim H} C_2H_2 \text{ (intramolecular)}$$

$$\upharpoonright C{\equiv}C \upharpoonright \xrightarrow{RH} HC_2\cdot \xrightarrow{RH} C_2H_2 \text{ (intermolecular)}$$

Vinylidene is known to be one of the precursors of acetylene in the photolysis of ethylene[15,16] and the

$$\begin{tikzcd}
H_2C{=}CH_2 \arrow[r, "h\nu"] & H_2C{=}C: + H_2 \arrow[d, "\sim H"] \\
& HC{\equiv}CH
\end{tikzcd}$$

ethynyl radical, produced from photolysis of bromoacetylene–nitric oxide mixtures, has been shown[17] to form acetylene by hydrogen abstraction from hydrocarbons.

$$\cdot C_2H + R{-}H \longrightarrow C_2H_2$$

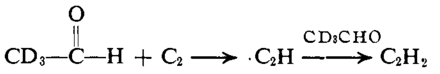
A. Reactions of C_2 with Acetaldehyde. To demonstrate the operation of both inter- and intramolecular reactions between C_2 and acetaldehyde, a reaction between carbon vapor and a mixture of acetaldehyde-d_0 and -d_4 was carried out. The same preference for an intramolecular process, $(C_2H_2 + C_2D_2) > 70\%$, as seen for acetone, was observed here (see Table II). Twice the yield of acetylene-d_1 is identified as the intermolecular portion of the reaction, 29%, and the remainder the intramolecular portion (71%). This is similar to the distribution between paths for the reactions of C_2 with acetone (25:75, *vida infra*) and benzene (18:82).[5]

Table II. Acetylene from Acetaldehyde-d_0/d_4 Mixture

Deuterium[a] content	Acetaldehyde,[b] mol %	Acetylene,[b] mol %
d_0	52.5	45.7
d_1	0.0	14.3
d_2	0.0	40.0
d_3	0.0	
d_4	47.5	

[a] Acetaldehyde analysis at 9.0 eV; acetylene at 11.0 eV. [b] Both acetylene and acetaldehyde are isotopically stable to the experimental conditions employed.

The –CHO hydrogens of aldehydes are the reactive sites[18] for H-atom transfers to radicals. The radical nature of the intermolecular process for acetaldehyde was demonstrated to involve the acyl hydrogen by carrying out the reaction of acetaldehyde-2,2,2-d_3 with C_2. From this system, acetylene-d_0 can only be an intermolecular product since it requires the attack of a C_2 molecule on the acyl hydrogens of two molecules of acetaldehyde. Table III shows the mass spectral analysis of the deuterated acetaldehyde and the resultant acetylene.



$$CD_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H + C_2 \longrightarrow \cdot C_2H \xrightarrow{CD_3CHO} C_2H_2$$

Table III. Acetylene from Acetaldehyde-2,2,2-d_3

Deuterium[a] content	Acetaldehyde, mol %	Acetylene,[b] mol %
d_0	0.0	28.0
d_1	0.4	22.7
d_2	5.0	49.3
d_3	94.6	
d_4	0.0	

[a] As in footnote *a*, Table II. [b] Uncorrected for 5% acetaldehyde-d_2.

The acetylene-d_0 present, 28%, accounts for all of the intermolecularity of the reaction (29%). This result indicates that processes involved in forming the intermolecular acetylene must have a high degree of radical character, a result consistent with the intermediacy not only of an enthynyl radical[17] but also a *triplet C_2 molecule*, both of which show a strong preference of abstraction of hydrogen from the –CHO function.

$$\cdot C{\equiv}C\cdot + CD_3CHO \longrightarrow CD_3\dot{C}O + HC{\equiv}C\cdot$$

$$HC{\equiv}C\cdot + CD_3CHO \longrightarrow CD_3\dot{C}O + HC{\equiv}CH$$

The equations depicting the reaction pathway require the presence of acetyl radicals. Since the acetyl

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(12) P. S. Skell and J. H. Plonka, *J. Amer. Chem. Soc.*, **92**, 836 (1970).

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

(14) J. Nichols, C. MacKay, and R. Wolfgang, *J. Amer. Chem. Soc.*, **88**, 1065 (1966).

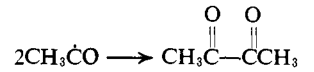
(15) M. C. Sauer, Jr., and L. M. Darfman, *J. Chem. Phys.*, **35**, 497 (1961).

(16) H. Okabe and J. R. McNesby, *ibid.*, **36**, 601 (1962).

(17) A. M. Tarr, O. P. Strausz, and H. E. Gunning, *Trans. Faraday Soc.*, **61**, 1946 (1965); **62**, 1221 (1966).

(18) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 279.

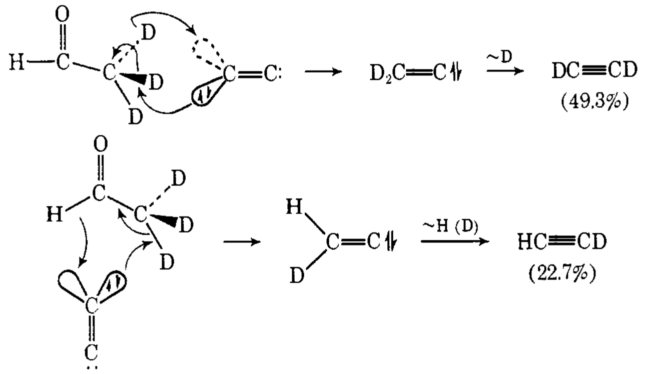
radical is stable[19] with respect to decomposition into carbon monoxide and methyl radicals at low temperature no methane should be produced. There is only a trace of methane present in the product mixture. However, 2,3-butanedione, the dimerization product, is formed in 17% yield (based on one molecule of C_2 producing one molecule of 2,3-butanedione).



$$2CH_3\dot{C}O \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}CH_3$$

Since the acetylene-d_0 accounts for all of the intermolecular portion of the reaction of C_2 with acetaldehyde-2,2,2-d_3, the acetylene-d_1 and -d_2 must arise by an intramolecular mechanism wherein a C_2 molecule abstracts two hydrogen atoms from one molecule of acetaldehyde. Such behavior would not be expected of a triplet species; there are no reports that triplet carbenes abstract two hydrogens intramolecularly.[20] This argument, coupled with the fact that a triplet vinylidene cannot rearrange to ground-state acetylene (whereas singlet alkyl carbenes rearrange readily[21,22]), leads us to favor the singlet ground state of C_2 as the precursor in the intramolecular path to acetylene. If this hypothesis is correct, the data in Table III require that there be two intramolecular mechanisms operative: 1,1-diabstraction as well as 1,2-diabstraction, both of which lead to a singlet vinylidene, as shown in Scheme I. The ratio of 1,1- to 1,2-diabstraction is 2.2.

Scheme I



Scheme I predicts that ketene should be a side product of 1,2-diabstraction directly or through the Wolff rearrangement of the acyl carbene formed from the 1,1-diabstraction, but no ketene could be isolated. Presumably, it dimerized or reacted with the acetaldehyde.[23]

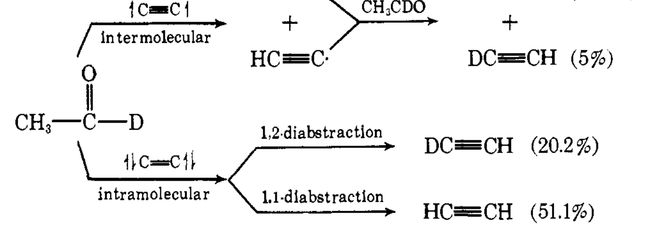
To examine the possibility that acetylene formation from acetaldehyde may be subject to isotope effects, the reaction of C_2 with acetaldehyde-1-d_1 was investigated. The composition of the recovered acetylene appears in Table IV. A comparison of these data with that given in Table III indicates a significant difference in the labeling pattern. Employing the same arguments used in the case of acetaldehyde-2,2,2-d_3, acetylene-d_2 must be an intermolecular product. If one assumes the previous value of 29% intermolecular reaction, the 5% missing from the acetylene-d_2 must be assigned to acetylene-d_1, formed by attack of triplet C_2 and/or $\dot{C}_2D$ on the methyl group of acetaldehyde 1-d_1. The separation into intra- and intermolecular paths is shown in Scheme II.

Table IV. Acetylene from Acetaldehyde-1-d_1

Deuterium[a] content	Acetaldehyde,[b] mol %	Acetylene, mol %
d_0	0.0	51.1
d_1	100.0	25.2
d_2	0.0	23.7
d_3	0.0	
d_4	0.0	

[a] As in footnote *a*, Table II. [b] Isotopic position shown by presence of P-2 peak and infrared spectra (see Experimental Section).

Scheme II



On a per hydrogen basis, the triplet $C_2 \rightarrow \cdot C_2H$ pathway (intermolecular) still shows a 14-fold (23.7 ÷ 5/3) greater reactivity of CDO over CH_3. With acetaldehyde-2,2,2-d_3, there was no discernible attack of C_2 on the methyl (±2%) but it should be noted that the labeling of the acetaldehydes is such that the isotope effects favor α attack in acetaldehyde-1-d_1 while opposing it in the acetaldehyde-2,2,2-d_3.

In the intramolecular (singlet) portion of the reaction with acetaldehyde-1-d_1, Scheme II shows that the ratio of 1,1- to 1,2-diabstraction is 2.5, to be compared with a value of 2.2 for acetaldehyde-2,2,2-d_3. Such a change corresponds to an isotope effect of 1.1 ± 0.1. Both reactions of singlet C_2 are insensitive to isotope substitution; the relative amount of 1,1- to 1,2-diabstraction is not determined by bond energies but perhaps by the spatial orientations of the collisions.

B. Reactions of C_2 with Acetone. Acetone also exhibits intra- and intermolecular modes of acetylene formation as determined from a reaction of C_2 with a mixture of acetone-d_0 and -d_6. The results of this experiment are given in Table V. Again, twice the

Table V. Acetylene from Acetone-d_0 and -d_6 Mixture

Deuterium[a] content	Acetone,[b] mol %	Acetylene,[b] mol %
d_0	55.3	51.0
d_1	0.0	12.3
d_2	0.0	36.7
d_3	0.0	
d_4	0.0	
d_5	0.0	
d_6	44.7	

[a] Determined by low voltage mass spectroscopy. [b] Both acetone and acetylene are isotopically stable to the reaction and work-up conditions.

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(19) E. O'Neal and S. W. Benson, *J. Chem. Phys.*, **36**, 2196 (1962).

(20) Both singlet and triplet methylene forms methane, but both processes occur by methyl radicals in intermolecular steps. See R. W. Carr, Jr., and G. B. Kistiakowsky, *J. Phys. Chem.*, **70**, 118 (1966), and M. L. Halberstadt and J. R. McNesby, *J. Chem. Phys.*, **45**, 1666, (1966). There is a report (see D. S. Breslow, T. J. Prosser, A. F. Marcantonio, and C. A. Genge, *J. Amer. Chem. Soc.*, **89**, 2384 (1967)) that triplet *n*-octadecyloxycarbonylnitrene may abstract two hydrogens from cyclohexane to form cyclohexene in an intramolecular manner.

(21) H. E. Zimmerman and J. H. Munch, *ibid.*, **90**, 187 (1968).

(22) I. Moritani, Y. Yamamoto, and S. I. Murahashi, *Tetrahedron Lett.*, 5697, 5755 (1968).

(23) D. G. Farnum, J. R. Johnson, R. E. Hess, T. B. Marshall, and B. Webster, *J. Amer. Chem. Soc.*, 87, 5191 (1965).

Table VI. Partitioning of Acetylene from CD_3COCH_3[a]

Deuterium content	Total acetylene,[b] mol %	Intermolecular,[c] mol %	Intramolecular,[d] mol %	Intramolecular normalized mol %
d_0	42.2	8.6	33.6	46
d_1	18.3	12.0	6.3	7
d_2	39.5	4.4	35.1	47

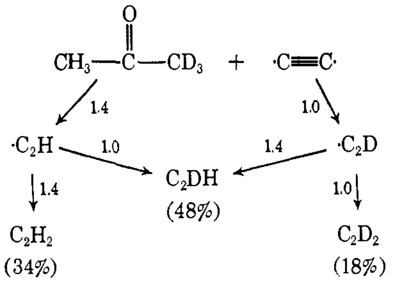
[a] Acetone is 90% labeled as shown (see Experimental Section). [b] Analysis at 11.0 eV. [c] Obtained by taking 0.25 × (mole fraction of d_n from Scheme III). [d] (Total acetylene-d_n) − (intermolecular acetylene-d_n).

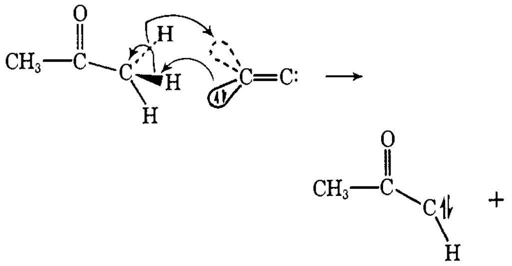
amount of acetylene-d_1 was taken as a measure of the intermolecularity of the reaction: for acetone 25% of the acetylene is produced by an intermolecular process. Approximately the same relative amounts of the singlet and triplet states are reacting to give acetylene (3 to 1) as in the acetaldehyde system.

While the data presented above for acetaldehyde required that both 1,1- and 1,2-diabstraction were important intramolecular paths to acetylene, a 1,2-diabstraction is impossible in the case of acetone; 1,1- and 1,3-diabstractions are possible. The mechanism of the intramolecular C_2 reaction with acetone was investigated using acetone-1,1,1-d_3 as a substrate.

After correction for the intermolecular portion of the reaction occurring with $k_H/k_D = 1.4$[24] (Scheme III) the residual acetylene must come from the intramolecular process (Table VI). For the intramolecular reaction, $(C_2H_2 + C_2D_2) \div C_2HD$ is the ratio of 1,1- to 1,3-diabstraction: 13.3.[25] There is a strong preference for 1,1-diabstraction of hydrogen to give singlet vinylidene and singlet acetylcarbene. This reaction occurs with $k_H/k_D = 1.0$.

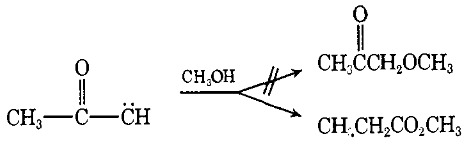
Scheme III





The prediction that methylketene should be formed for the Wolff rearrangement of acetylcarbene, as in the case of acetaldehyde, could not be substantiated.

No methylketene could be isolated directly from the reaction mixture; however, when a mixture of 33% acetone and 67% methanol was used as the reactive matrix, methyl propionate could be recovered from the trapping of methylketene by methanol[26] and methoxyacetone was not present in the reaction mixture.[27] The ester was formed in 4% yield, a substantial amount considering that C_2 also reacts with methanol.[3] Since the Wolff rearrangement requires a singlet precursor, singlet acetylcarbene,[28] and rearrangement of vinylidene requires a singlet vinylidene, it follows from spin conservation considerations[29] that the reaction was initiated by a *singlet C_2 molecule.*



Conclusions

On the basis of the evidence presented in this paper, it appears that the C_2 molecule possesses different chemical properties which depend upon the multiplicity of the C_2. The triplet form of C_2 reacts in an intermolecular manner and exhibits a radical selectivity in hydrogen abstraction, correlated with bond energy. The singlet C_2 species reacts in an intramolecular manner to produce singlet vinylidene in an unselective manner. The singlet form prefers a 1,1-diabstraction mechanism. While 1,2-diabstraction is significant, 1,3-diabstraction is not. In the cases of acetaldehyde and acetone, the relative amounts of triplet and singlet C_2 molecules reacting to form acetylene are 27 and 73 ± 2%, respectively, despite the large difference in carbon–hydrogen bond energies: -CHO, 78 kcal/mol,[30] and CH_3CO–, 92 kcal/mol.[31]

Experimental Section

Diatomic carbon is produced simultaneously with C_1, C_3, and C_4 in the reaction system previously described.[32] All arcing was done at 16 V (ac). The general reaction procedure outlined below is also applicable to the examination of the chemistry of any vapor component. The reaction system is evacuated by a large floor pump

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(24) To make this separation, an isotope effect of 1.4 is assumed for both steps. The work with acetaldehyde (see above) indicates an overall isotope effect for triplet $C_2 \rightarrow C_2H_2$ of 1.2, a reaction with a much weaker carbon–hydrogen bond than is found in acetone. The isotope effect assumed for acetone is the same one found by Gunning and Strausz[17] for the reaction of $\cdot C_2H$ with alkanes.

(25) This is a minimum value since any mixing of the labels during synthesis would have contributed C_2HD by the 1,1-intramolecular route. The acetone is isotopically stable to the carbon vapor reaction conditions.

(26) Methyl propionate is not a product of carbon vapor plus methanol.

(27) It has been shown that acetyldiazomethane photolyzed in a methanol matrix at −196° gives only methyl propionate and no methoxyacetone, indicating the Wolff rearrangement is facile under the reaction conditions. See P. S. Skell, J. H. Plonka, and L. S. Wood, *Chem. Commun.*, 710 (1970).

(28) M. Jones, Jr., and W. Ando, *J. Amer. Chem. Soc.*, **90**, 2200 (1968).

(29) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).

(30) J. R. Majer, C. R. Patric, and J. C. Robb, *Trans. Faraday Soc.*, **57**, 14 (1961).

(31) J. A. Kerr, *Chem. Rev.*, **66**, 496 (1966).

(32) P. S. Skell, L. Wescott, Jr., J. P. Golstein, and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 2829 (1965).

with a pumping speed of 15 ft^3/min and an oil diffusion pump with a speed of 160 l./sec at 10^{-5} Torr. The pumping system is separated from the reaction flask by a liquid nitrogen trap which prevents intercontamination. With the reaction system evacuated to $\sim 10^{-4}$ Torr by the large floor pump, the two graphite electrodes are butted together and degassed by resistive heating at $\sim$1400°. The degassing process is terminated when the pressure again falls to the 10^{-4} Torr range; the electrodes are then separated. Liquid nitrogen is then added to the trap protecting the pumping system and the oil diffusion pump is turned on. The reaction flask is then submerged in liquid nitrogen and pumping continued until a pressure of $\sim 5 \times 10^{-6}$ Torr is reached. With a voltage of 16 V across the still separated electrodes, previously degassed substrate is allowed to enter the flask through a gas flow meter at a rate of 0.5 to 1.0 g/min. The inlet ring mounted inside the reactor directs the incoming substrate away from the arc zone to the walls of the reactor. This method of deposition makes on the walls a cylindrical band of substrate, 3 in. high, with 2.5-in. radius having the arc at its center. After a layer of substrate has accumulated on the walls of the reactor (5 min), the electrodes are touched to strike an arc; substrate and carbon vapor are simultaneously cocondensed on the walls of the reaction flask. Arcing is continued intermittently, maintaining a pressure of less than 10^{-4} Torr. The normal deposition rate of carbon vapor is 1–2 mg/min, but compounds which produce carbon monoxide during the deposition require a slower rate of vapor deposition. The codeposition is continued until 30–60 mg of carbon has been vaporized. Arcing is then terminated and the reactor isolated from the high-speed pumping system. The liquid nitrogen coolant is removed and the substrate–product mixture is transferred to a vacuum line for product isolation by trap-to-trap distillation and gas chromatography.

Carbon-14 reactions are run according to the above procedure, with the exception that the lower electrode is replaced with a carbon-14 enriched graphite rod ($^1/_2$ in. long $\times$ $^1/_8$ in. diameter; 3.4 mCi/rod). These rods were purchased from the United Kingdom Atomic Energy Authority. The activity measurements were obtained with an ionization chamber (Cary No. 5010) according to a literature procedure.[33] Attachment of the ionization chamber to the exit port of a gas chromatograph allowed the determination of the molar activity of each eluting component.

The deuterium content of the acetylene samples reported was determined by low-voltage mass spectroscopy on a Nuclide G-12-90 mass spectrometer. Isotopic stability of the materials examined was checked by subjecting the compounds to analysis before and after their exposure to the reaction conditions.

Acetone-d_6, acetaldehyde-d_4, and ethanol-1,1-d_2 employed were purchased from Volk Radiochemicals and used as received. The D_2O employed in exchanges was purchased from Stohler Isotopic Chemicals.

Acetaldehyde-2,2,2-d_3. This compound was prepared by the exchange with D_2O using pyridine as a catalyst.[34] The nmr spectrum showed a sharp singlet at τ 0.30 for the acyl hydrogen. The mass spectral analysis is given in Table III.

Acetaldehyde-1-d_1. This compound was prepared by dissolving 180 g (0.29 mol) of ceric ammonium nitrate in 375 ml of H_2O and adding 15 g (0.31 mol) of CH_3CD_2OH. The solution was heated on a steam bath under N_2 with 0° reflux condensor until the red color disappeared.

Trap-to-trap distillation of the reaction mixture under vacuum gave 9.0 g (0.2 mol) of the acetaldehyde.

The nmr spectrum showed no peak at τ 0.30 for acyl hydrogen. The mass spectrum showed a base peak at $m/e = 45$ with peaks at $m/e = 43$ (CH_3CO^+) and $m/e = 30$ (CDO^+). The infrared spectrum showed no band at 3.6 μ and was identical with a literature spectrum of acetaldehyde-1-d_1.[35]

Acetone-1,1,1-d_3. The trideuterioacetone was prepared by the method outlined by Dellepiane and Overend.[36] The Grignard reagent of methyl iodide was added to acetaldehyde-2,2,2-d_3 to make 1,1,1-trideuterio-2-propanol. The deuterated propanol was converted to the triisopropoxyaluminum compound and oxidized with benzophenone. A detailed experimental procedure for these conversions is available.[37] The purity of the recovered acetone was determined by an examination of its mass spectrum fragmentation pattern.[36] The properly labeled compound would give only $m/e = 46$ ($C_2D_3O^+$) and $m/e = 43$ ($C_2H_3O^+$) ions while $m/e = 45$ and 44 are derived from other labeled isomers. The relative intensities of these ions at 15 eV were

m/e	Rel intensity
46	100.0
45	5.5
44	4.8
43	94.8

indicating an isotopic purity of 90%. The infrared spectrum of the deuterated acetone was identical with the literature spectrum.[36]

Methyl propionate and 2,3-butanedione were identified by mixed glc and combined glc mass spectroscopy. The absence of methoxyacetone was established by the failure to observe a peak of the proper retention time.

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