C_2H_4 production under conditions ($E \leqslant -1.35$ V) where reduction of **1** is mass-transport controlled.

Control experiments demonstrate that both a Mo(III) species and an additional source of electrons (or H_2) are required for acetylene reduction. Electrolysis of C_2H_2 alone at $E \leqslant -1.35$ V in borate buffer and in the presence of substances which strongly catalyze H_2 evolution (e.g., cysteine) produces no C_2H_4 or C_2H_6. Thus, the H_2 evolved at the cathode does not reduce C_2H_2 directly. When a solution of **1** is prereduced, purged with C_2H_2, and allowed to stand with no potential applied, ethylene forms only very slowly (Table I, condition D). If potential is reapplied, ethylene production resumes at the rate indicated under condition B. This result and the potential dependence of the rate of C_2H_4 formation suggest that a simple redox reaction between reduced Mo catalyst and C_2H_2 producing C_2H_4 and an oxidized Mo species may not be the principal means of acetylene reduction.

We believe the primary function of the Mo(III) catalyst is to bind acetylene as a substrate. Although we have been unable to isolate an intermediate or confirm its presence by uv-visible spectroscopy, some interaction between Mo(III) and C_2H_2 must occur because reduction of acetylene, even in the presence of H_2 evolution, does not proceed unless molybdenum is present. The proposed $Mo^{III} \cdot C_2H_2$ adduct may produce C_2H_4 and C_2H_6 through routes which do not involve a simple Mo(V) $\rightleftarrows$ Mo(III) redox cycle. These alternative routes include: (1) addition of electrons to bound C_2H_2 from an external source (electrode or chemical reductant) followed by protonation, (2) insertion of H_2 or hydride into the adduct in a manner similar to known homogeneous hydrogenation reactions,[16] and (3) electrocatalytic hydrogenation of the adduct by adsorbed H atoms produced on the electrode surface. Mechanisms 1 and 2 could be operative in both the chemical and electrochemical models, whereas mechanism 3 would be restricted to the electrochemical system.

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(6) Ichikawa and Meshitsuka[5] also noted formation of ethylene when complex **1** was reduced at a graphite cathode in the presence of acetylene. However, no details of the process were reported.

(7) Controlled potential electrolysis was carried out in 0.1 *F* $Na_2B_4O_7$ at a stirred Hg pool cathode (11.5 cm^2 area) in a sealed cell equipped with a gas sampling port. Solution and gas phase volumes in the cell were 45 and 85 ml, respectively. Acetylene was washed with water before purging through the cell.

(8) Hydrocarbons were analyzed by gas chromatography on a 5 ft × 0.25 in. Porapak N column at ambient temperature with thermal conductivity detection. Yields were corrected for hydrocarbon solubilities in the aqueous phase.

(9) Experiments with solutions containing K_3MoCl_6 and cysteine were performed to provide additional evidence that a Mo(III) species is the active catalyst. Our further remarks are confined to acetylene reduction catalyzed by the electrochemical reduction product of complex **1**.

(10) A referee has suggested that the equilibrium $Mo(III)_2 \rightleftarrows Mo(II) + Mo(IV)$ also could explain the half-order dependence of C_2H_4 formation on total Mo concentration. However, despite recent reports[11-14] of low-valent Mo complexes in aqueous solution, existence of such an equilibrium has yet to be demonstrated, and we have no evidence to indicate that Mo(II) or Mo(IV) is formed in our solutions.

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CF_2 Emission in the Reaction between Ozone and Tetrafluoroethene

Sir:

We report here a strong luminescence in the reaction of O_3 with C_2F_4 which we identify as due to CF_2. To our knowledge, this is the first time that emission from electronically excited CF_2 has been detected in a chemically reacting system.

Pure ozone was prepared by passing ozonized oxygen (Matheson Ultrapure grade) through a silica gel trap at −78°, replacing the oxygen carrier with helium, and allowing the trap to warm to room temperature. For some experiments an oxygen carrier was used. The carrier flowed at approximately 20 μmol sec^{-1} and a pressure of 45 Torr into a reaction vessel at room temperature where it was mixed with C_2F_4 (Columbia Organic Chemicals). The $[O_3]$ was monitored from its absorbance at 254 nm and both reactant gas pressures were ~1 Torr. A Jarrell-Ash 0.25-m monochromator with a spectral slit width of 0.8 nm and a 2360 grooves/mm grating blazed at 300 nm viewed the reaction vessel axially through a quartz window. Photomultipliers used were an EMI 9781IR and an EMI 9683QKB both at −78°.

A few experiments were carried out for comparative purposes on the luminescence of O_3 with ethylene, 1,1-difluoroethene, *cis*-1,2-difluoroethene, *trans*-1,2-difluoroethene, and hexafluoropropene. All substrates were distilled before use.

Total emission was measured for with the monochromator removed, and the results, uncorrected for the photomultiplier spectral response, are given in Table I. The emission from the C_2F_4-O_3 system, unlike that from the other systems, was entirely within the uv and extended from 245 to 400 nm with resolved peaks from 250 to 355 nm.

A typical spectrum in the presence and absence of O_2 is shown in Figure 1 and shows the dramatic quenching effect of O_2. The peaks from the O_3-C_2F_4 emission are listed in Table II. In addition, a weak unidentified visible luminescence with peaks at 490, 506, 520, 525, 539, 560, 580, 595, 604, and 625 was detected by removing the second-order uv spectrum with a Kodak Wrattan 2A filter. These peaks were not affected by using an oxygen carrier.

Table I. Relative Total Intensities for Ozone Chemiluminescence

Reactant	Intensity relative to C_2H_4	Approximate λ_{max}, nm
C_2H_4	1	450
C_2F_4	545	320
1,1-$C_2H_2F_2$	1.2	440
cis-1,2-$C_2H_2F_2$	20	440
trans-1,2-$C_2H_2F_2$	26	440
C_3F_6	0.8	—

Table II. Comparison of Bands of CF_2

$10^{-3}\bar{\nu}_{vac}$,[a] cm^{-1}	$10^{-3}\bar{\nu}_{vac}$,[b] cm^{-1}	$10^{-3}\bar{\nu}_{vac}$,[a] cm^{-1}	$10^{-3}\bar{\nu}_{vac}$,[c] cm^{-1}	$10^{-3}\bar{\nu}_{vac}$,[b] cm^{-1}	$10^{-3}\bar{\nu}_{vac}$,[c] cm^{-1}	$10^{-3}\bar{\nu}_{vac}$,[b] cm^{-1}
41.667		35.869		35.86	30.615	30.63
41.491		35.706		35.69	30.457	30.44
41.168		35.540		35.54	30.309	30.33
40.996		35.208		35.21	30.277	
40.677		35.047		35.06	30.171	
40.509		34.880			30.110	30.07
40.436		34.715			29.963	29.95
40.184		34.550		34.57	29.811	29.79
39.946		34.384		34.41	29.657	29.62
39.692	39.70	34.222		34.24	29.623	
39.514		34.060			29.507	
39.339		33.891		33.88	29.471	29.45
39.195	39.16	33.559		33.57	29.310	29.29
39.023		33.394		33.36	29.172	29.13
38.851		33.240		33.23	28.973	29.00
38.695	38.67	33.073			28.824	28.81
38.530	38.55	32.906		32.91	28.673	28.66
38.525		32.738		32.77	28.530	28.51
38.352		32.568		32.55	28.396	28.37
38.187	38.20	32.410		32.45	28.327	28.28
38.033	38.04		32.255		28.178	28.18
37.691	37.70		32.081	32.10	28.024	*e*
37.535	37.53		31.917	31.93	27.956	
37.366	37.36		31.738	31.76	27.885	
37.189		31.590			27.752	
37.039	36.98	31.428		31.37	27.683	
36.872	36.85	31.265		31.24	27.535	
36.534	36.52	31.104		31.10	27.385	
36.365	36.35	30.940			27.234	
36.205	36.21	30.765		30.71	27.098	
36.036					*d*	

[a] Reference 1. [b] This work. [c] Reference 7. [d] Bands continue to 23808 cm^{-1}. [e] Weak continuum to ~25000 cm^{-1}.

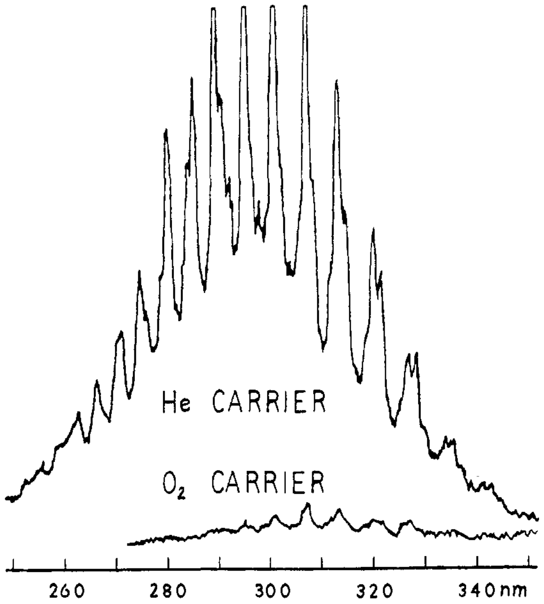

Figure 1. Typical spectrum of uv emission from the O_3-C_2F_4 system. Total pressure ~45 Torr.

Venkateswarlu[1] observed bands from 240 to 325 nm in emission from a CF_4 discharge which he attributed to CF_2 and for which he gave vibrational assignments. Subsequent investigations of the absorption spectrum revealed the same bands[2-5] which were reassigned in terms of bending frequencies.[3] Marsigny et al.[6,7] have obtained bands in emission from a discharge extending to 420 nm which they have ascribed to CF_2. Table II gives a comparison of the data of Venkateswarlu, Marsigny et al., and this work. Some higher energy vibronic bands observed in the emission from a discharge are absent in our system apparently due to insufficient reaction exothermicity. Other vibronic bands, especially at the longer wavelengths, are not observed due to the low intensity.

Our average discrepancy with the data of Venkateswarlu is 5 cm^{-1}, and with the data of Marsigny et al. it is 11 cm^{-1}. These values are less than the estimated error limits of ± 15 cm^{-1} of our monochromator.

The gas phase reaction between O_3 and C_2F_4 was studied by Heicklen[8] with O_3 kept in excess. The products were COF_2 and O_2 only, and no epoxide or ozonide formation was found. Gozzo and Camaggi[9] carried out the reaction in the liquid and gas phases and found no O_2 was formed when C_2F_4 was in excess. They gave the stoichiometry as $2C_2F_4 + O_3 \rightarrow 2COF_2 + C_2F_4O$. Interestingly, they postulated the formation of CF_2 as follows: $C_2F_4 + O_3 \rightarrow (C_2F_4O_3) \rightarrow COF_2 + CF_2O_2$, $CF_2O_2 \rightarrow CF_2 + O_2$. However, this sequence is only 72 ± 8 kcal mol^{-1} exothermic, which is far short of the 117 kcal mol^{-1} required here. The energy needed for emission at $\lambda \geq 245$ nm must come from additional secondary reactions. These secondary reactions are probably quenched by O_2 (see Figure 1), for CF_2 although long-lived[5] does not in its ground (singlet) state appear to react with O_2 at room temperature.[10] The kinetics of the system are currently being investigated.

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Vacuum-Ultraviolet Photolysis of $C_2(CH_3)_6$, $Si_2(CH_3)_6$, and $(CH_3)_3CSi(CH_3)_3$. Evidence for an Unsaturated Silicon-Carbon Linkage

Sir:

We have initiated studies on the vacuum-ultraviolet photochemistry of gas phase peralkylated silanes and their hydrocarbon analogues. While at this point only relative yields of fragments containing 17 atoms or less are available, the paucity of data of this type and the current interest in silicon-containing reactive intermediates prompt us to communicate our preliminary results.

Hexamethyldisilane, hexamethylethane, and *tert*-butyltrimethylsilane[1] were photolyzed using a xenon resonance lamp (147 nm) under a variety of conditions. Each of the three compounds was photolyzed as a pure gas at its vapor pressure (approximately 10 Torr in each case) and in the presence of 10% oxygen. Additionally, hexamethylethane was photolyzed as part of a mixture (containing O_2 and CF_4) over the range of pressures 1-760 Torr. All photolyses were terminated after $\leq 0.1\%$ conversion of parent to product.

Table I summarizes product yields in each experiment. In samples in which oxygen was added, products whose yield decreased to zero or near zero are interpreted as arising from bimolecular reactions involving at least one free radical intermediate.[2] Products remaining in scavenged systems are interpreted as arising from unimolecular reactions, either as direct products of the photolysis or as secondary decomposition products from species containing excess internal energy.

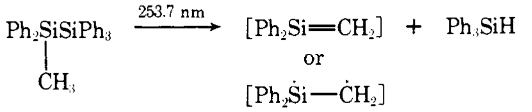
Our primary motivation in this work was to compare the probability of developing a silicon-carbon double bond or its equivalent relative to that of forming a carbon-carbon double bond under similar conditions.

In the vacuum-ultraviolet photolysis of alkanes containing more than one kind of hydrogen, the elimination of alkanes by the transfer of a primary hydrogen, particularly via a four-centered transition state as compared to a three-center transition state, is of low probability.[3] Nonetheless, it can be seen from Table I that the production of isobutane from hexamethylethane is of considerable importance. The addition of oxygen to remove radical sources of isobutane leaves a significant yield of this hydrogen transfer product. Apparently the removal of other reaction pathways and the large number of equivalent hydrogens available for transfer enhances the importance of this reaction as an exit path from the excited state of hexamethylethane.

The only similar reactions reported for the photochemistry of silicon containing compounds are:

$$CH_3SiH_3 \xrightarrow[\text{or 123 nm}]{\text{147 nm}} [\dot{C}H_2\dot{S}iH_2] + H_2 \qquad (1)$$

and



$$Ph_2Si(CH_3)SiPh_3 \xrightarrow{\text{253.7 nm}} [Ph_2Si{=}CH_2] \text{ or } [Ph_2\dot{S}i{-}\dot{C}H_2] + Ph_3SiH \qquad (2)$$

In their discussion of reaction 1, Obi, et al., refer to $[CH_2SiH_2]$ as a diradical rather than assigning olefinic character to the species.[4] The reactive intermediate produced from pentaphenylmethyldisilane on the other hand, was described as a silicon-carbon double bond or its equivalent which then undergoes rapid addition to methanol-d_1.[5]

The photolysis of hexamethyldisilane in the presence of oxygen clearly establishes the importance of a hydrogen transfer reaction, as trimethylsilane is the most important stable fragmentation product. The absence of the silicon analogue to isobutene is not surprising in view of its demonstrated high reactivity.[6] While our work does not allow us to comment on the electronic configuration of the "unsaturated" carbon-silicon moiety, it does allow for a comparison of the probability of its production relative to the formation of a carbon-carbon double bond.

Photolyzing *tert*-butyltrimethylsilane provides an opportunity to form an unsaturated cofragment, isobutene, when hydrogen transfer occurs to form trimethylsilane. This is formally the reverse of the well-known hydrosilation reaction.[7] At the same time there is an opportunity to form isobutane, a process observed to give an unsaturated cofragment in the photolysis of hexamethylethane, in such a way that the cofragment contains silicon. These two possibilities may be represented as:

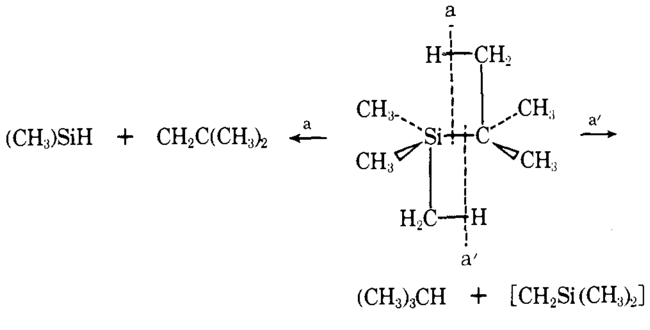


Table I. Relative Quantum Yields of Several Fragments Produced by the Photolysis of $C_2(CH_3)_6$, $Si_2(CH_3)_6$, and $(CH_3)_3CSi(CH_3)_3$

Product/system	$C_2(CH_3)_6$[a]	$C_2(CH_3)_6 + O_2$	$Si_2(CH_3)_6$	$Si_2(CH_3)_6 + O_2$	$(CH_3)_3CSi(CH_3)_3$	$CH_3CSi(CH_3)_3 + O_2$
CH_4	0.46	0.47	0.12	0.21	0.55	0.61
C_2H_6	0.50	—	0.28	—	0.4	0.04
C_3H_6	0.61	1.2	—	—	0.09	0.08
i-C_4H_{10}	1.0	1.0	—	—	1.0	1.0
$(CH_3)_3SiH$	—	—	1.0	1.0	0.6	0.48
i-C_4H_8	2.0	3.3	—	—	1.3	1.04
neo-C_5H_{10}	0.4	—	—	—	0.18	—
$Si(CH_3)_4$	—	—	0.33	—	0.10	—
Yields given relative to:	*i*-C_4H_{10}	*i*-C_4H_{10}	$(CH_3)_3SiH$	$(CH_3)_3SiH$	*i*-C_4H_{10}	*i*-C_4H_{10}

[a] Traces of C_2H_4, C_2H_2, C_3H_8, and C_3H_4 were also observed, yields $<0.10 \times$ *i*-C_4H_{10}-