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 - In a typical experiment, 1 ml of a 9% solution of **2** in benzene was injected (0.5 drop/sec) into a quartz tube (55 \times 0.9 cm) with a nitrogen flow (30 cm³/min). **1** was separated from the pyrolysate (which contained undecomposed **2**, 1–2% ethyl carbamate, and an as yet unidentified component), by gas chromatography (5 ft \times 0.25 in., 15% SE-30 on 80/100 Chromosorb W at 80°).
 - The yield, which has not been optimized, was based on unrecovered **2** and was sensitive to the surface of the pyrolysis tube.
 - The iminolactone **2** is very sensitive to moisture and did not consistently give reproducible values of the ultraviolet spectral parameters. The extinction coefficient is an average of several experiments ($\pm 20\%$).
 - In support of this hypothesis, Kricheldorf¹¹ has reported the facile isomerization of a β -isocyanatoacrylate to an alkoxy-1,3-oxazin-6-one.
 - Steglich et al.¹¹ have furnished examples of thermal conversions of derivatives of **9** to 1,3-oxazin-6-ones.
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 - These results parallel an earlier report by Maier³ of a derivative of **1**.

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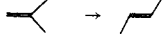

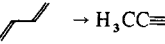
Concerning Criticisms of MINDO/3 by Pople¹ and Hehre²

Sir:

Pople¹ bases his criticisms of MINDO/3³ on calculated heats of reaction for 16 processes, mostly artificial, in 11 of which the errors in the MINDO/3 values are large. This is not surprising since they involve three compounds (CH₄, C(CH₃)₄, CH₃C≡CCH₃) for which the errors in the MINDO/3 heats of formation are unusually great. Since we not only tabulated the errors in our papers but also drew specific attention to them in the text,⁴ it is not clear to us what further point Pople is trying to make.

The Hartree-Fock values cited by Pople¹ were derived from 6-31 G* or 4-31 G calculations of energies of molecules, using assumed geometries. We might point out that there seems to be no difficulty in getting reasonably accurate estimates of molecular energies by semiempirical methods if one is willing to make such assumptions. This is illustrated in Table I by a comparison of Pople's results for his 16 reactions with those calculated by MINDO/1.⁵ The standard deviations for the nine reactions for which data are available by both methods are 3.22 (HF) and 1.75 (MINDO/1) kcal/mol, respectively. Note that MINDO/1 represented only a preliminary version. We did not pursue this approach further because of the limited scope of a treatment in which geometries are not optimized. With re-

Table I. Comparison of Errors in Heats of Reaction Calculated by ab Initio SCF and MINDO/1 Methods

| Reaction | Error in calcd heat of reaction (kcal/mol) | |
|---|--|---------|
| | "Hartree-Fock" | MINDO/1 |
| CH ₃ CH ₃ + H ₂ → 2CH ₄ | -6.4 | +0.2 |
| CH ₂ =CH ₂ + 2CH ₄ → 2CH ₃ CH ₃ | -5.3 | -1.6 |
| HC≡CH + 4CH ₄ → 3CH ₃ CH ₃ | -12.1 | - |
| CH ₃ CH ₂ CH ₃ + CH ₄ → 2CH ₃ CH ₃ | -1.2 | 0.0 |
| CH ₃ (CH ₂) ₂ CH ₃ + 2CH ₄ → 3CH ₃ CH ₃ | -4.0 | -1.1 |
| CH ₃ (CH ₂) ₃ CH ₃ + 3CH ₄ → 4CH ₃ CH ₃ | - | -1.4 |
| CH ₃ CH=CH ₂ + CH ₄ → CH ₃ CH ₂ + CH ₂ =CH ₂ | -1.3 | +1.0 |
| CH ₃ C≡CH + CH ₄ → CH ₃ CH + HC≡CH | 0.4 | - |
| H ₂ C=C=CH ₂ + CH ₄ → 2CH ₂ =CH ₂ | -1.2 | - |
| CH ₃ CH=CH ₂ → Δ | 0.0 | +3.3 |
| CH ₃ C≡CH → Δ | 3.5 | - |
| CH(CH ₃) ₃ → n-C ₄ H ₁₀ | 1.5 | -0.4 |
| C(CH ₃) ₄ → n-C ₅ H ₁₂ | - | +1.4 |
|  →  | -1.0 | +1.6 |
|  → H ₃ CC≡CCH ₃ | -2.1 | - |
| C ₆ H ₆ + 6CH ₄ → 3CH ₃ CH ₃ + 3CH ₂ CH ₂ | +1.4 | +3.0 |

gard to ref 2, it is surprising that no reference is made to calculations of bond lengths. Moreover the major errors he cites again occur in cases to which we have drawn specific attention in our papers.

Since very extensive tests of MINDO/3 have been published,³ including applications to a wide variety of chemical reactions,⁶ there seems no need for further comment.⁷

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- See in particular Figures 2 and 3 of part XXV,^{3a} Table I of part XXVI,^{3b} Table I of part XXVII,^{3c} Table I of part XXVIII,^{3d} Table I of part XXIX,^{3e} and the discussions on pp 1292,^{3a} 1294,^{3b} 1302,^{3c} 1309–1310,^{3d} and 1313.^{3e}
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- EDITOR'S NOTE: This communication should have appeared concurrently with the communications cited in ref 1 and 2, but was inadvertently delayed in editorial processing.

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Catalytic Electrochemical Reduction of Acetylene in the Presence of a Molybdenum-Cysteine Complex

Sir:

A chemical model for nitrogenase enzyme¹ based on the binuclear molybdenum(V)-cysteine complex, Na₂Mo₂O₄(Cys)₂ (**1**),² has been shown to be effective in the catalytic reduction of nitrogenase substrates. A Mo(IV)-cysteine monomer, produced by reduction of **1** with NaBH₄ or Na₂S₂O₄, has been proposed^{1b} as the active species responsible for binding and reducing substrates such as acetylene.

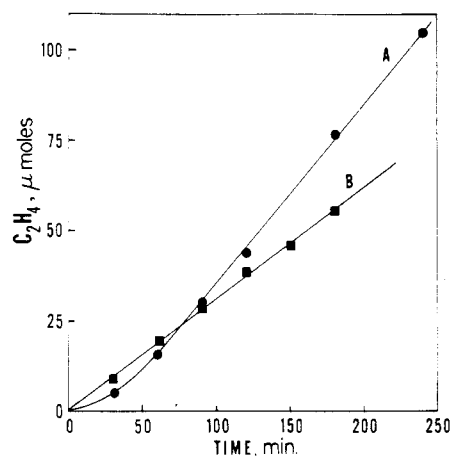


Figure 1. Ethylene formation under conditions A and B: 1 mM **1**, 1 atm of C₂H₂, $E_{app} = -1.40$ V, 0.1 F Na₂B₄O₇, pH 9.2.

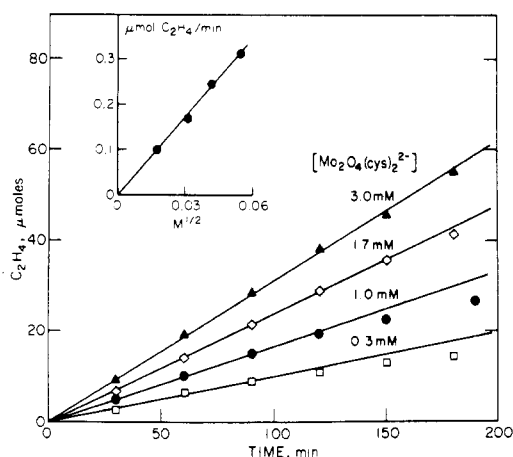


Figure 2. Ethylene formation during electrolysis of reduced complex **1** in the presence of 1 atm of C₂H₂ (condition B, Table I): $E_{app} = -1.40$ V, 0.1 F Na₂B₄O₇, pH 9.2. Inset: rate of C₂H₄ formation vs. $[1]^{1/2}$.

We have recently reported on the electrochemical reduction of **1**³ and similar di- μ -oxo-bridged Mo(V) complexes⁴ under solution conditions comparable to the chemical model studies (pH 8–10 borate buffer). These complexes are reduced in a single four-electron step at -1.2 to -1.3 V vs. SCE to Mo(III) products with no evidence of an intermediate oxidation state. Our electrochemical results suggest that polarographic evidence⁵ previously cited¹⁸ as confirmation of a Mo(IV) catalyst is incorrect, and that the authors of ref 5 have mistakenly identified the electrochemical reduction of **1** as a Mo(V) \rightarrow Mo(IV) rather than a Mo(V) \rightarrow Mo(III) process.

In this report we present results on the electrochemical reduction of **1** in the presence of acetylene and on the nature of the species responsible for the catalytic reduction of C₂H₂ to C₂H₄ and C₂H₆.⁶ These results provide the first evidence that a *monomeric Mo(III) complex* is the catalytically active species in chemical models for nitrogenase enzyme based on Mo–thiol complexes.

Electrochemically catalyzed reduction of acetylene has been achieved under three conditions:^{7,8} (A) controlled potential electrolysis of **1** at -1.35 to -1.5 V under 1 atm of C₂H₂, (B) prerduction of **1** to the Mo(III) state followed by purging with 1 atm of C₂H₂ and reapplication of potential, and (C) application of negative potential (-1.4 V) to a 1:1 solution of Mo(III) (added as K₃MoCl₆) and cysteine under 1 atm of C₂H₂. Involvement of Mo(III) is established by the fact that acetylene reduction occurs during electro-

Table I. Rate of Ethylene Formation and Final Product Ratio

| Condition ^a | E_{app} , V | Rate | |
|------------------------|---------------|---|---|
| | | (mol of C ₂ H ₄ /min) | C ₂ H ₄ :C ₂ H ₆ ^b |
| A | -1.35 | 1.80×10^{-7} | 5.7 |
| A | -1.40 | 2.64×10^{-7} | 4.9 |
| A | -1.50 | 4.58×10^{-7} | 5.6 |
| B | -1.40 | 1.85×10^{-7} | 5.4 |
| C | -1.40 | 1.33×10^{-7} | 4.7 |
| D | No E | 3.8×10^{-9} | — |

^a Conditions: (A) 1 atm of C₂H₂ present initially, 1 mM **1**; (B) 1 atm of C₂H₂ added after reduction of 1 mM **1**, potential reapplied; (C) 1 atm of C₂H₂ added to 2 mM K₃MoCl₆ + 2 mM cysteine, potential applied; (D) 1 atm of C₂H₂ added after reduction of 1 mM **1**, no potential applied. All experiments conducted in 45 ml of 0.1 F Na₂B₄O₇, pH 9.2. ^b Measured after 180 min.

chemical reduction of **1** by two electrons per Mo. In addition, electrolysis of solutions containing equimolar Mo(III) and cysteine catalyzes acetylene reduction at approximately the same rate. It is not likely that reduction proceeds beyond Mo(III) in formation of the active catalyst, because electrochemically reduced solutions of **1** and solutions of K₃MoCl₆ and cysteine exhibit no voltammetric reduction peaks.

Representative data are shown in Table I and Figures 1 and 2.⁹ Acetylene reduction occurs during electrolysis of the initial complex under condition A. The rate of ethylene formation does not reach a constant value until 20–40 min (required for mass-transport controlled reduction of **1**) have elapsed (Figure 1). Thereafter under condition A, and at all times under condition B, C₂H₄ appearance is linear with time for at least 180 min. After approximately 3 hr, catalytic activity diminishes slightly as indicated by a decrease in the rate of C₂H₄ production. However, the system still achieves true catalytic behavior after 6–8 hr, even under the most stringent assumption that all of the Mo present is converted to catalytically active monomer.

Ethane also is produced during electrolysis. The C₂H₄:C₂H₆ ratio decreases from 10:1 to a constant value of ca. 5:1 after 30–60 min.

The square-root dependence of the rate of ethylene formation on concentration of **1** (Figure 2) demonstrates that the active catalyst is a monomeric species in equilibrium with a larger fraction of dimeric material. We have previously investigated³ the dissociation reaction of the binuclear reduction product of **1**. The rate-determining step in this process involves cleavage of one of the μ -oxo bridge bonds to form a mono-oxo-bridged dimer. Further reactions responsible for formation of the proposed monomeric catalyst have not been clearly delineated. However, the mono-oxo-bridged dimer could either be in direct equilibrium with a Mo(III) monomer or dissociate to a Mo(III) monomer in equilibrium with a further dimeric species. Either interpretation is consistent with our previous results and the present observation of a monomeric Mo(III) catalyst.¹⁰

The rate of ethylene formation increases with either an increase in negative potential (Table I) or a decrease in pH. Both changes also lead to an increase in catalytic hydrogen evolution, which occurs concurrently with acetylene reduction. The electrode reaction product of **1** strongly catalyzes H₂ evolution at a mercury electrode. Evolution of H₂ in the absence of substrates other than H⁺ is an important feature of both the chemical model system¹ and nitrogenase enzyme.¹⁵ In the present system the charge owing to H₂ evolution exceeds by 10–20 times the quantity of charge required to produce the observed amounts of reduced hydrocarbons. However, an important relationship between H₂ evolution and C₂H₂ reduction is indicated by the effect of electrode potential, which markedly affects the rate of

C_2H_4 production under conditions ($E \leq -1.35$ 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 $E \leq -1.35$ 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 prerduced, 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 $Mo(V) \rightleftharpoons Mo(III)$ 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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- (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 \times 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 $Mo(III)_2 \rightleftharpoons Mo(II) + Mo(IV)$ also could explain the half-order dependence of C_2H_4 formation on total Mo concentration. However, despite recent reports¹¹⁻¹⁴ 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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CF₂ 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 $20 \mu\text{mol sec}^{-1}$ 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 |
| <i>cis</i> -1,2- $C_2H_2F_2$ | 20 | 440 |
| <i>trans</i> -1,2- $C_2H_2F_2$ | 26 | 440 |
| C_3F_6 | 0.8 | — |