

or not at all if the oxidation state is high. A similar behavior has been noted for molecules like CO and NO on metal surfaces; the binding is substantially reduced if the surface is partially oxidized, for example, with a halogen: cf. L. Lynds, *Spectrochim. Acta*, **20**, 1369 (1964); C. R. Guerra and J. H. Schulman, *Surf. Sci.*, **1**, 229 (1967); M. Kobayashi and T. Shirasaki, *J. Catal.*, **28**, 289 (1973); R. A. Della Betta, *J. Phys. Chem.*, **79**, 2519 (1975); M. F. Brown and R. D. Gonzalez, *ibid.*, **80**, 1731 (1976); A. A. Davydov and A. T. Bell, submitted for publication in *J. Catal.*

- (27) The chamber contamination problem for a molecule like iodine can be minimized with a crystal isolation cell.²⁰ At the low pressures employed in these displacement reactions, the thermodynamic probability of reaction between the chemisorbed molecule and reactants like I₂ or (CN)₂ typically will be low.
- (28) For example, R. C. Batezold, *Adv. Catal.*, **25**, 1 (1976); J. C. Robertson and C. W. Wilmsen, *J. Vac. Sci. Technol.*, **9**, 901 (1972).
- (29) In (η⁶-C₆H₆)₂M molecules like Cr(C₆H₆)₂, one of the two arenes can be displaced by strong field, 2-electron donor molecules like phosphines, but this displacement requires high temperatures and photochemical activation (M. G. Thomas, L. F. Stuhl, and E. L. Muetterties, unpublished observations). Displacements of η⁶-arene ligands from molecules like C₆H₆ML₃ have not been reported for 2-electron donor molecules but are well established for 6-electron, more basic arene molecules at elevated temperatures.
- (30) M. G. Thomas, W. R. Pretzer, B. F. Beier, F. J. Hirsekorn, and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 743 (1977); E. L. Muetterties, E. Band, W. R. Pretzer, M. C. Thomas, and A. Kokorin, to be published.
- (31) We have initiated a study of displacement reactions with metal clusters to establish displacement series for 2-electron donor ligands, 4-electron donor ligands as typified by acetylenes bound as in **1**, etc.
- (32) To probe the possibility of rearrangement of a molecule on chemisorption to an isomer, i.e., a new molecule, it is important that the chemisorption behavior of isomers be examined. Thus, a chemisorption study of, for example, 2-butyne should be complemented with studies of the isomers 1-butyne, methylallene, and 1,3-butadiene. If all four C₄H₆ isomers chemisorb without isomerization, their chemisorbed states will be differentiable (diffraction, spectroscopic, and displacement reaction characteristics). Recently we have demonstrated that CH₃CN and CH₃NC chemisorb on Ni(111) without isomerization to CH₃CN and CH₃CN, respectively.⁹ CH₃CN is the more thermodynamically stable isomer of the two.
- (33) A. J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1415 (1974).
- (34) In fact, mesitylene behaves differently from benzene on the (111) and (110) faces of platinum (J. L. Gland and G. A. Somorjai, *Surf. Sci.*, **41**, 387 (1974); *Adv. Colloid Interface Sci.*, **5**, 203 (1976)).
- (35) Structural definition of molecular fragments chemisorbed on a metal surface is far more difficult than for a molecular species. If hydrogen is present or is presumed to be present in the fragment as is the case for the important hydrocarbon fragments, a compositional characterization of the chemisorbed fragment cannot be accurately achieved. However, reactions of such chemisorbed fragments might yield desorbed reaction products that could provide a structural characterization. In some cases, it would be necessary to raise the pressure of the reaction system orders of magnitude above those for the typical displacement-type reaction to thermodynamically allow the desired reaction. For example, a CH₂ species now demonstrated in cluster chemistry (R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **99**, 5225 (1977)) and probably preparable as a chemisorbed species from CH₂N₂ and a metal surface might react with cyanogen on a surface to give CH₂(CN)₂; a methyl fragment might react with cyanogen to give acetonitrile (a molecule weakly bound at a surface), and a benzyne might react with bromine to give *o*-C₆H₄Br₂ (surface bound benzyne probably will not generally flash desorb as benzyne because of the thermal reactivity of the remaining C-H hydrogen atoms).
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Received June 28, 1977

The Apparent Demise of a Model Reaction for Aldehyde Oxidase

AIC706039

Sir:

A recent model for the mechanisms of the reactions of certain molybdoenzymes involves the transfer of an oxygen atom between the substrate and a molybdenum atom in the

Table I. Reactions of MoO₂(Etcys)₂^a with Benzaldehyde^b in Various Solvents

Solvent	Time, h	mol of C ₆ H ₅ CHO consumed/mol of complex	mol of 1a recovered ^c /mol of complex
DMF ^d	18	1.5	1.3
DMF ^d	95	1.5	
DMF ^{d,e}	18	1.5	1.3
DMF ^{d,f}	18	1.0 ^g	1.2 ^h
Me ₂ SO ^d	94	0.8	
CH ₂ Cl ₂ ⁱ	71	1.9	1.6

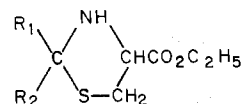
^a 0.11 M. ^b 0.45 M. ^c Recovery accomplished by removing the solvent by vacuum distillation followed by extraction of the residue with ether. ^d Loss of benzaldehyde followed by VPC on 1/8 in. × 6 ft column packed with Porapak Q using toluene or *o*-xylene as an internal standard. ^e Contained 0.08 M benzoic acid. ^f Contained 2.5 M water. ^g No further consumption of benzaldehyde occurred after an additional reaction time of 17 h. ^h Although this value exceeds the consumption of benzaldehyde, it undoubtedly results from shifting the equilibrium toward products due to the removal of water along with solvent in the recovery of **1a**. ⁱ As in footnote ^d, but using Chromosorb 101.

enzyme.^{1,2} Besides the obvious facts that oxomolybdenum species are dominant in an aqueous environment, that reduction tends to decrease the number of oxygen atoms that are bound to molybdenum, and that substrate reactants and products differ by only a single oxygen atom, two model reactions provided impetus for proposing this mechanism. The first is the well-studied abstraction of an oxygen atom from oxomolybdenum complexes by various phosphines.^{3,4} The second, which is shown in reaction 1, is the brief report of the

$$2\text{MoO}_2(\text{Etcys})_2 + \text{RCHO} \rightarrow \text{Mo}_2\text{O}_3(\text{Etcys})_4 + \text{RCOOH} \quad (1)$$

oxidation of aldehydes with MoO₂(Etcys)₂ (Etcys = L-C₂H₅OOCCH(NH₂)CH₂S⁻) in either DMF or Me₂SO to give the corresponding carboxylic acid and Mo₂O₃(Etcys)₄.⁵ Mimicry of an aldehyde oxidase was apparently achieved and a plausible mechanism based on the transfer of an oxygen atom to the substrate has been postulated.² However, this reaction can only be regarded as tenuous since neither the nature of the aldehydes nor the experimental details were given. We must now provide evidence which refutes reaction 1 at least under one set of experimental conditions.

Using the experimental conditions which are given in Table I, we have examined the reaction between benzaldehyde and MoO₂(Etcys)₂ under rigorously air-free conditions at room temperature. The solvents were either DMF, Me₂SO, or CH₂Cl₂. The reaction remains homogeneous only when DMF or Me₂SO are used leading to amber-brown (green when water is present intentionally in large quantities) and green solutions, respectively. When the reaction is conducted in CH₂Cl₂, a blue precipitate containing molybdenum forms. Although we have not yet been able to identify this product,⁶ we have not observed the intense purple color of Mo₂O₃(Etcys)₄ at any time during the course of these reactions.⁷ Furthermore, no resonances due to the phenyl hydrogen atoms of benzoic acid were observed in the NMR spectra which were recorded at the completion of a reaction although it would have been possible to do so if that compound were present in reasonable quantities. The high yields of the diastereomeric esters of phenylthiazolidine, **1a**, which were recovered point to the conden-



1a, R₁ = C₆H₅, R₂ = H
b, R₁ = *n*-C₈H₁₇, R₂ = H
c, R₁ = R₂ = CH₃

Table II. Reactions of $\text{Mo}_2\text{O}_3(\text{Etcys})_4^a$ with Carbonyl Substrates^b in CH_2Cl_2

Substrate	Time, h	mol of substrate consumed ^c / mol of complex	mol of $\text{Mo}_2\text{O}_4(\text{Etcys})_2^d$ / mol of complex
$\text{C}_6\text{H}_5\text{CHO}$	28	2.0	0.9
<i>n</i> - $\text{C}_5\text{H}_{11}\text{CHO}$	1.5	2.3	0.5
CH_3COCH_3	120	1.5	0.8

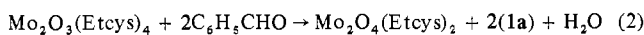
^a 0.057 M. ^b 0.29 M. ^c Loss of substrate followed by VPC. Conditions were identical with those given in Table I for benzaldehyde and hexanal. A column of identical dimensions packed with 3% Carbowax on Gas Chrom-Q was used with acetone. ^d Recovery accomplished by filtration.

sation of the aldehyde with the bound amino acid esters as the major and possibly only pathway of this reaction. Characterization of the thiazolidine was accomplished in all cases, even when yields were not measured, by comparing the infrared and NMR spectra of the product to those of an authentic sample.⁹

Although other interpretations are possible, the best explanation of the data may well be a solvent-dependent equilibrium which differs in the various solvents only in the extent of solvation of the molybdenum product. If so, the equilibrium position in DMF is strongly dependent upon the deliberate presence of water, a logical product (along with the formation of an additional MoO linkage⁶) when more than one amino acid ester is used. The equilibrium position is also independent of the presence of benzoic acid, the product which would result from reaction 1. The reaction in Me_2SO , which is slower than that in DMF, was not followed to completion. The increased use of benzaldehyde in CH_2Cl_2 may occur because of poor solvation and the resulting precipitation of the molybdenum product.

The condensation of a ligand with an aldehyde is not confined¹⁰ to the reaction with benzaldehyde. A far more rapid reaction occurs between hexanal (0.49 M) and $\text{MoO}_2(\text{Etcys})_2$ (0.12 M) in CH_2Cl_2 . After only 5 min, 1.9 ± 0.2 mol of hexanal/mol of $\text{MoO}_2(\text{Etcys})_2$ was consumed, as shown from sequential integrations of the NMR resonance, due to the aldehydic hydrogen atom. No further consumption of hexanal was found between 5 and 15 min nor did we find any evidence for either hexanoic acid, using either NMR or VPC, or a purple color. Thiazolidine **1b**, which was recovered in essentially quantitative yields, was again characterized by comparing its infrared and NMR spectra to those of an authentic sample.⁹

The presumed product of reaction 1, $\text{Mo}_2\text{O}_3(\text{Etcys})_4$, also reacts with these aldehydes as well as acetone as shown in Table II. The products from these reactions are $\text{Mo}_2\text{O}_4(\text{Etcys})_2$, at least initially, and the corresponding thiazolidines. The latter were isolated and identified in each case. The reaction with benzaldehyde was again slow and clearly conformed to reaction 2. The reaction with hexanal was again



fast and occurred in at least two steps. The first step is equivalent to reaction 2. However, it is clear from the data in Table II that the consumption of hexanal is larger than that of benzaldehyde while the recovery of $\text{Mo}_2\text{O}_4(\text{Etcys})_2$ is less. These results suggest that the latter is also capable of a reasonably fast reaction with hexanal. Indeed, when $\text{Mo}_2\text{O}_4(\text{Etcys})_2$ (0.042 M) and hexanal (0.42 M) were stirred in CH_2Cl_2 for 5 h, both of the remaining ligands were stripped from the complex since quantitative consumption of the aldehyde was observed. An unidentified, partially soluble, brown precipitate which contained molybdenum was also present.

The thiazolidine in the filtrate was positively identified. Finally, the reaction of $\text{Mo}_2\text{O}_3(\text{Etcys})_4$ with acetone results in the formation of $\text{Mo}_2\text{O}_4(\text{Etcys})_2$ and **1c**. This reaction explains Melby's synthesis⁸ of the latter from $\text{Mo}_2\text{O}_3(\text{Etcys})_4$ in acetone.

We also note that when $\text{MoO}_2(\text{S}_2\text{CNET}_2)_2$ was stirred with hexanal in CH_2Cl_2 for 24 h, no detectable quantities of hexanoic acid were observed. The analogous reaction with acetaldehyde has been predicted to have a favorable enthalpy change (ca. -40 kcal mol⁻¹) according to thermochemical cycles.¹¹ No significant differences in the predicted value of ΔH are expected when hexanal is substituted for acetaldehyde. Furthermore, there are indications that entropic terms are small for analogous reactions so that $\Delta H^\circ \approx \Delta G^\circ$.¹¹ Similarly, it would appear that $\text{MoO}_2(\text{S}_2\text{P}(\text{OEt})_2)_2$ might be unstable toward reduction since that compound has not been isolated in the solid state and can only be generated in solution from the disproportionation of $\text{Mo}_2\text{O}_3(\text{S}_2\text{P}(\text{OEt})_2)_4$.¹² However, when the latter was stirred with hexanal in CH_2Cl_2 for 24 h, no reaction occurred.

While the results obtained for $\text{MoO}_2(\text{Etcys})_2$, $\text{MoO}_2(\text{S}_2\text{CNET}_2)_2$, or $\text{Mo}_2\text{O}_3(\text{S}_2\text{P}(\text{OEt})_2)_4$ do not invalidate a mechanism for aldehyde oxidase based on the transfer of an oxygen atom, neither are they encouraging. Nevertheless, one positive affirmation results from the attempted reaction of $\text{MoO}_2(\text{S}_2\text{CNET}_2)_2$ with hexanal, a reaction which is presumed to be thermodynamically favorable. Activation of either the aldehyde or the complex will be required in order to obtain a favorable rate for the transfer of an oxygen atom.¹³

Acknowledgment. Support for this research was provided by NSF Grant No. MPS 75-08188.

Registry No. Aldehyde oxidase, 9029-07-6; $\text{MoO}_2(\text{Etcys})_2$, 22775-78-6; hexanal, 66-25-1; benzaldehyde, 100-52-7; **1a**, 64331-74-4; **1b**, 64331-73-3; **1c**, 64331-72-2; acetone, 67-64-1; $\text{Mo}_2\text{O}_3(\text{Etcys})_4$, 24228-97-5.

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- The infrared spectrum of this product contains three broad bands at 950, 910, and 850 cm⁻¹ which are probably due to Mo=O stretching vibrations and another at 720 cm⁻¹ which might be attributed to the Mo-O-Mo group. The spectrum also contains weak absorptions due to water and a carboxyl group. The latter appears to result from the presence of small quantities of either **1a** or bound amino acid ester which has not reacted. The color of the product suggests that it may be a member of the family of molybdenum blues. If so, the origin of the required reducing equivalents is unknown.
- We can readily estimate the maximum concentration of $\text{Mo}_2\text{O}_3(\text{Etcys})_4$ which could have been present in the CH_2Cl_2 from existing data. The band primarily responsible for the purple color occurs at 504 nm with ϵ 13 500 M⁻¹ cm⁻¹ in CHCl_3 .⁸ We judge conservatively that $\text{Mo}_2\text{O}_3(\text{Etcys})_4$ in concentrations less than 10⁻⁵ M may have escaped visual detection under the experimental conditions where the path length (flask diameter) was approximately 5 cm. This estimate is based on the reasonable assumption that the extinction coefficients in CH_2Cl_2 and CHCl_3 are similar. Since the original concentration of $\text{MoO}_2(\text{Etcys})_2$ was 0.11 M (see Table I), only a very minor fraction of the molybdenum could have been present as $\text{Mo}_2\text{O}_3(\text{Etcys})_4$ at any time during the course of the reaction.
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- Samples of the required thiazolidines were prepared from the aldehyde or ketone and the ethyl ester of L-cysteine.
- We have also observed that the reaction of acetaldehyde with $\text{MoO}_2(\text{Etcys})_2$ produces the required thiazolidine without the appearance of either acetic acid or a purple color. Nevertheless, side reactions certainly occur since 7.5 equiv of the aldehyde was used. This reaction may well involve self-condensation of the aldehyde.
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- (13) Photochemical activation of the $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$ -benzaldehyde system and the formation of benzoic acid have been reported by C. C. Garner, R. Durant, and F. E. Mabbs, *Inorg. Chim. Acta*, **24**, L29 (1977), shortly before the publication of our paper. An examination of the $\text{MoO}_2(\text{EtOys})_2$ -benzaldehyde system in the absence of photolysis is also reported briefly. Although conditions were not specified, they claim no reaction occurs in CH_2Cl_2 . However, the initial yellow solution in DMF became pink after several hours but then paler with the precipitation of diethylcystine and without the formation of benzoic acid. These results differ considerably from our own observations which include the results reported herein as well as the additional observations that diethylcystine is a liquid (at least we have not been able to achieve crystallization at this point) which is extremely soluble in DMF. Nevertheless, their

observations have caused us to suggest that the blue precipitate obtained⁶ from our reaction in CH_2Cl_2 may result from partial reduction of Mo(VI) by small amounts of the ligand. The results quoted in Table I for this reaction would not invalidate this proposal.

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Received August 8, 1977

Additions and Corrections

1976, Volume 15

John I. Gelder and John H. Enemark*: Crystal and Molecular Structure of Tetra-*n*-butylammonium Di- μ -sulfido-bis(oxo-1,1-dicyanoethylene-2,2-dithiolatomolybdate(V)), $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_2\text{O}_2\text{S}_2(\text{S}_2\text{C}_2(\text{CN})_2)_2]$.

Page 1839. The value of γ for the working triclinic cell given in the abstract and the experimental section is wrong and should be $\gamma = 104.62^\circ$.

Page 1839. In column two, line 17 should have $a_r = a_w + b_w$ in place of $a_r = a_w - b_w$.

Page 1840. In Table III entry Mo1-O2 should read Mo2-O2.—John H. Enemark

R. H. Niswander and L. T. Taylor*: Structural Changes in Cobalt(II) Complexes Resulting from Nonsteric Substituent Effects with Potentially Five-Coordinate Ligands.

Pages 2361 and 2362. Figures 1 and 2 are reversed.—R. H. Niswander

1977, Volume 16

Roger E. Cramer,* Steven W. Cramer, Katherine F. Cramer, Mary Ann Chudyk, and Karl Seff: Redetermination of the Crystal and Molecular Structure of *trans*-Diaquobis(2,4-pentanedione)nickel(II) Perchlorate, Including Location and Refinement of Hydrogen Atoms.

Pages 220 and 222. The captions for Figures 1 and 2 are interchanged.—Roger E. Cramer