Specific Enhancement of Catalytic Activity of Molybdenum(V)–Cysteine Complex for Acetylene Reduction in the Presence of Various Charge Carriers

Sir:

Molybdenum(V)–thiol complexes have been reported[1] to play a specific role as a nonprotein model for nitrogenase (N_2-ase) in the reduction of N_2-ase substrates. Schrauzer, *et al.*, recently demonstrated[2] that some metal salts such as $FeSO_4$ could have a cocatalytic effect to stimulate the catalytic efficiency of the Mo(V)–cysteine complex, but the cocatalytic activity ceased after some time. The function of the additives is still unsolved.

In order to simulate the role of a non-heme Fe protein as a charge carrier in the N_2-ase system by a simple model, we performed experiments on the cocatalytic effects of organic and organometallic charge carriers on the catalytic activity of a Mo(V)–cysteine complex for acetylene reduction. It was found that the charge carriers with reduction potentials around −0.9 V *vs.* saturated H_2 electrode ("she") specifically enhanced the catalytic reduction of acetylene by the Mo(V)–cysteine complex by three–seven times. It was assumed that the activation by the charge carriers was associated not only with facilitating inefficient charge transfer from reductants such as $NaBH_4$ and $Na_2S_2O_4$ to Mo(V) sites but also with the generation of reactive hydrogen in the reaction system. A typical experiment for the cocatalytic effects due to the addition of charge carriers is as follows. When acetylene (0.5 atm) was admitted onto an alkaline solution (40 cm³, pH 9.6 borate buffer) of $Na_2Mo_2O_4(Cys)_2 \cdot 5H_2O$ (0.42 mmol) (Cys = cysteine) and $NaBH_4$ (1.0 mmol) at 27°, ethylene was selectively formed[3] with a trace of ethane and hydrogen at rates similar to those reported by Schrauzer, *et al.*[2] By adding a catalytic amount of various charge carriers (*ca.* 0.17 mmol) such as water soluble herbicides (bipyridyl diquaternary salts), phthalocyanines, and quinones to the reaction system of the Mo(V)–cysteine complex and $NaBH_4$, the rate of ethylene formation instantaneously increased by one–seven times, depending on the added charge carriers. A similar enhancement of ethylene formation was also confirmed when the additives were charged into the reaction system just before acetylene was injected. Acetylene reduction hardly took place without molybdenum (Na_2MoO_4) in a solution of each additive and $NaBH_4$, even when cysteine was added to the solution.[4] It seems reasonable to suppose that these additives act as cocatalysts for stimulating the catalytic activity of the Mo(V)–cysteine complex for acetylene reduction. In the absence of acetylene in the reaction system the hydrogen evolution was considerably enhanced by addition of these carriers.

In Figure 1, the relative effects of various charge carriers on the acetylene reduction by Mo(V)–cysteine complex are plotted against the reduction potentials of the corresponding additives, which were determined by polarography using a mercury electrode in a pH 9.6 borate buffer solution at 27°. It is interesting to note that an optimum enhancement of ethylene formation was observed for the additives having reduction potentials around −0.9 V *vs.* "she," and lower enhancements for the additives with lower or higher reduction potentials. A similar optimum region (—●—) was found when various transition metal salts were employed[5] as charge carriers, as also shown in Figure 1.

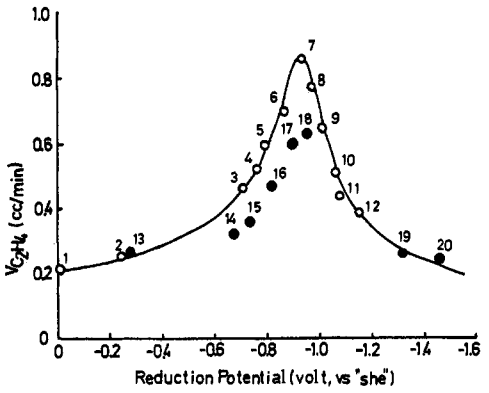

Figure 1. The cocatalytic effects of various charge carriers on acetylene reduction by the Mo(V)–cysteine complex (0.42 mmol) and $NaBH_4$ (1.0 mmol), plotted against the reduction potentials (volt *vs.* "she") of the corresponding additives, where $V_{C_2H_4}$ denotes the rate of ethylene formation when each charge carrier (0.17 mmol) was added to the reaction system. In the absence of the charge carriers, the rate of ethylene formation was *ca.* 0.16 cm³/min in a solution of $Na_2Mo_2O_4(Cys)_2$ and $NaBH_4$ under the similar reaction conditions. For the bipyridyl diquaternary salts and phthalocyanines, the second-reduction potentials are taken from the polarographic results: (1) Methylene Blue, (2) sodium riboflavin phosphate, (3) 1,1′-ethylene-4,4′-dimethyl-2-2′-bipyridylium bromide, (4) 2,2′-bipyridylium chloride, (5) 1,1′-dimethyl-4,4′-bipyridylium bromide, (6) 2,2′-bipyridylium-1,1′-ethylene-5,5′-dimethyl bromide, (7) 1,1′-trimethylene-2,2′-bipyridylium bromide, (8) iron phthalocyanine-4,4′,4″,4‴-tetrasulfonate sodium, (9) copper phthalocyanine-4-(sodium sulfite), (10) metal-free phthalocyanine-4-(sodium sulfite), (11) $Fe^{2+}(bipy)_3SO_4$, (12) sodium anthraquinone-1-sulfonate, (13) $CuSO_4$, (14) $NiCl_2$, (15) $CoCl_2$, (16) $CdSO_4$, (17) $FeSO_4$, (18) $RhCl_3$, (19) $CrCl_3$, (20) $MnCl_2$.

Cocatalytic behavior of the water soluble herbicides and phthalocyanines could be repeated several times without appreciable decrease of activity upon additional injection of fresh $NaBH_4$. Through the reaction, the charge carriers were rapidly reduced by $NaBH_4$ to give mono- and dianions of the corresponding compounds, which were identified by the characteristic visible absorption spectra.

The catalytic activity of the Mo(V)–cysteine complex was similarly stimulated with the addition of these additives when $Na_2S_2O_4$ was employed instead of $NaBH_4$ as a reductant. For the transition metal salts, however, the enhancement ceased completely after each run, probably due to the irreversible reduction to an insoluble metal with $NaBH_4$ or $Na_2S_2O_4$ in an alkaline solution.

It was also demonstrated by the polarographic mea-

(1) G. N. Schrauzer and G. Schlesinger, *J. Amer. Chem. Soc.*, **92**, 1808 (1970).

(2) G. N. Schrauzer and P. A. Doemeny, *ibid.*, **93**, 1608 (1971); G. N. Schrauzer, P. A. Doemeny, G. W. Kiefer, and R. H. Frazier, *ibid.*, **94**, 3604 (1972).

(3) Gas mixture products were quantitatively analyzed by gas chromatography using a treated Al_2O_3 column at 0°.

(4) For the exceptional cases, a mixture of ethylene and ethane was formed very slowly (less than 0.01 cm³/min at 27°) in alkaline solutions of iron phthalocyanine tetrasulfonate and $RhCl_3$ (0.42 mmol) with $NaBH_4$ (1.0 mmol). No enhancement of ethylene formation was observed when cysteine (0.5 mmol) was added to the solutions.

(5) Similar results have been reported by Schrauzer, *et al.*,[2] on the enhancements of acetylene reduction by Mo(V)–cysteine complexes by transition metal salts such as $FeSO_4$.

surements[6] that the Mo(V)–cysteine complex ($Na_2Mo_2O_4(Cys)_2$) was reversibly reduced at −0.33 V (Mo(VI) ⇄ Mo(V)), −1.03 V (Mo(V) ⇆ Mo(IV)), and −1.9 V (Mo(IV) ⇄ Mo(III)), *vs.* "she" in a borate or carbonate (Na_2CO_3–$NaHCO_3$) buffer solution (pH 9.6, 27°) on a mercury electrode. When 0.5 atm of acetylene was admitted onto the solution of $Na_2Mo_2O_4(Cys)_2$ (pH 9.6 borate buffer, 27°) and the cathodic voltage from 0 to −2.0 V *vs.* a saturated calomel electrode ("sce") was applied to an inactive graphite electrode,[7] the selective ethylene formation occurred with cathodic voltage higher than −0.9 V *vs.* "she" (−1.14 V *vs.* "sce"). A considerable amount of hydrogen gas was also evolved at the graphite electrode at the cathodic voltage around −0.9 V *vs.* "she" in the absence of acetylene. The reduction of water proceeds in an alkaline solution as follows[8]

$$2H_2O + 2e^- = H_2 + 2OH^- \qquad (E_0 = -0.828 \text{ V } vs. \text{ "she"})$$

It was accordingly concluded that the charge carriers which have redox potentials around −0.9 V *vs.* "she" enhanced not only the charge transfer from the strong donors such as $NaBH_4$ and $Na_2S_2O_4$ to the Mo(V)–cysteine complex (it may facilitate the reduction of Mo(V) to Mo(IV) as an active state for acetylene reduction) but also the activation of hydride in $NaBH_4$ solution to produce reactive hydrogen, which could be responsible for the specific enhancement of catalytic efficiency of the Mo(V)–cysteine complex in the presence of charge carriers.

(6) $Na_2Mo_2O_4(Cys)_2 \cdot 5H_2O$ was dissolved in a borate buffer solution (0.05 g/50 cm³) and the *i*–*E* curves were observed under N_2 atmosphere at 27° with reference to the calomel electrode connected with a KCl salt bridge.

(7) In the absence of the Mo(V)–cysteine complex, acetylene was reduced to a mixture of ethylene and ethane (molar ratio *ca.* 4:1) at much lower rates (less than one-tenth of those with Mo(V)–cysteine present) at the cathodic voltages higher than −1.2 V *vs.* "sce."

(8) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, New York, N. Y., 1938.

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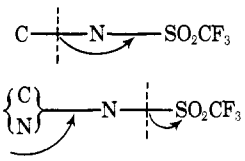
Triflamides ($CF_3SO_2N<$). A Survey

Sir:

The sulfonyl group offers unusually versatile reactivity in its capability of acting both as electrophile– and nucleophile–leaving group as well as its electron-withdrawing power to stabilize adjacent anions. These modes of reaction are all enhanced if the electron withdrawal is enhanced. Hence, we have surveyed the reactivity of trifluoromethanesulfonyl[1] (CF_3SO_2–; "trifyl") on nitrogen and carbon. The former, the triflamides, are generally stable, crystalline soluble sulfonamides quantitatively prepared[2] from amines with the anhydride $(CF_3SO_2)_2O$.[1] The acidity of primary triflamides is indicated by their solubility in bicarbonate ($CF_3SO_2NH_2$, pK_a = 5.8).

(1) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 4069 (1957).

(2) The structures assigned are supported by ir, nmr, and mass spectral evidence as well as elemental analyses. In general these were all clean, high-yield reactions in which, however, no effort was made to optimize yields.



(1)

(2)

Two kinds of cleavages of triflamides may be envisioned, as summarized in eq 1 and 2. The first of these has been examined for SN2 displacements of triflamide as stabilized leaving group[3] and displacement is facile only if two trifyl residues are present on the nitrogen. In corroboration we found benzyltriflimide, $C_6H_5CH_2N(SO_2CF_3)_2$, readily converted to benzyl bromide and methyl ether with bromide and methoxide ions. We observed the analogous elimination when isobutylene bubbled quantitatively from a bis triflation of *tert*-butylamine at −78°, *i.e.*, eq 3.

$$2(CF_3SO_2)_2O + (CH_3)_3CNH_2 \xrightarrow{NaH} [(CH_3)_3CN(SO_2CF_3)_2] \longrightarrow CH_2{=}C(CH_3)_2 + HN(SO_2CF_3)_2 \quad (3)$$

Cleavage 1 of acyl monotriflamides is very rapid, as evidenced by fast basic hydrolysis, ethanolysis, and aminolysis of the acyl group at room temperature. The acyl derivatives $RCON(C_6H_5)SO_2CF_3$ are cleanly prepared in high yield by treating $C_6H_5NHSO_2CF_3$ (mp 66–67°) with acid chlorides and triethylamine in methylene chloride (R = CH_3, mp 93–94°, 97%; R = C_6H_5, mp 97–98°, 85%; R = $C_6H_5CH{=}CH$, mp 109°, 85%)[2]; the acyltriflamides are somewhat less reactive than acyl chlorides and offer some advantages (*cf.* the otherwise difficult N-acetylation of pyrrole proceeds smoothly with $CH_3CON(C_6H_5)SO_2CF_3$).[4] Conversely, amides are readily N-triflated; caprolactam was converted to the salt with *tert*-butyllithium in benzene at 0° to form the cyclic acyltriflamide (mp 134–135°, 93%),[2] which was rapidly opened to the ester $CF_3SO_2NH(CH_2)_4COOCH_3$ with methoxide–methanol at room temperature.

$$RCH_2N(C_6H_5)SO_2CF_3 \xrightarrow{B:} RCH{=}NC_6H_5 + CF_3SO_2{:}^- \quad (4)$$

a, R = *p*-BrC_6H_4CO (mp 144–145°)
b, R = C_6H_5 (mp 79–80°)
c, R = *n*-C_4H_9 (oil)

Elimination of trifluoromethanesulfinate ("triflinate" anion from nitrogen (eq 2)) was examined in three representative cases with varying activation of the α proton. The models were all made by smooth room-temperature alkylation of phenyltriflamide in potassium carbonate–acetone.[2] The first case (**a**) was transformed into *p*-bromphenacylidene anil (mp 59–61°; lit.[5] 60–61°; 90%) on long stirring (or brief reflux) with K_2CO_3 in acetone.[6] The second case (**b**) was unreactive to prolonged boiling with K_2CO_3 in acetone but eliminated smoothly in 3 hr at 100° with NaH in dimethylformamide; aniline and benzaldehyde were isolated in over 80% yield following mild acid hydrolysis.

(3) (a) R. S. Glass, *Chem. Commun.*, 1546 (1971); (b) P. J. DeChristopher, G. D. Lyon, J. P. Adamek, R. J. Swedo, S. A. Klein, and R. J. Baumgarten, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1971, No. 14 (see also *J. Amer. Chem. Soc.*, **91**, 2384 (1969)).

(4) P. Keehn and J. Haley, private communication.

(5) W. A. Malik, D. R. Gupta, and C. L. Taploo, *J. Indian Chem. Soc.*, **46**, 253 (1969).

(6) By contrast the toluenesulfonamide was stable to several days boiling (K_2CO_3–acetone).