

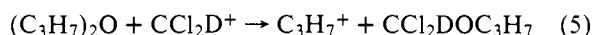
Table I. Observed Reactions and Rate Coefficients for the Reactions $\text{CCl}_2\text{D}^+ + \text{M} \rightarrow \text{Products}$

	Rel PA	Observed reactions	$k_{\text{total}} \times 10^{10a}$
$(\text{CH}_3)_2\text{O}$	-11.4^b	$\text{CCl}_2\text{D}^+ + (\text{CH}_3)_2\text{O} \rightarrow \text{CH}_3\text{OCH}_2^+ + \text{CCl}_2\text{DH}$	4.0 ± 1.0
$(\text{CH}_3)_2\text{S}$	-4.9^b	$\text{CCl}_2\text{D}^+ + (\text{CH}_3)_2\text{S} \rightarrow \text{CH}_3\text{SCH}_2^+ + \text{CCl}_2\text{DH}$	14.9 ± 2.0
$(\text{C}_2\text{H}_5)_2\text{O}$	-4.8^c	$\text{CCl}_2\text{D}^+ + (\text{C}_2\text{H}_5)_2\text{O} \rightarrow (\text{C}_2\text{H}_5)_2\text{OD}^+ + \text{CCl}_2$ (22%) $\rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_4^+ + \text{CCl}_2\text{DH}$ (78%)	12.5 ± 3.5
$(n\text{-C}_3\text{H}_7)_2\text{O}$	-3.2^c	$\text{CCl}_2\text{D}^+ + (n\text{-C}_3\text{H}_7)_2\text{O} \rightarrow \text{C}_3\text{H}_7^+ + \text{C}_3\text{H}_7\text{OC}_2\text{H}_5$ (100%)	12.8 ± 2.5
$\text{C}_2\text{H}_5\text{SCH}_3$	-1.8^c	$\text{CCl}_2\text{D}^+ + \text{C}_2\text{H}_5\text{SCH}_3 \rightarrow \text{CH}_3\text{SC}_2\text{H}_4^+ + \text{CCl}_2\text{DH}$ (~100%)	
NH_3	0.0^d	$\text{CCl}_2\text{D}^+ + \text{NH}_3 \rightarrow \text{NH}_3\text{D}^+ + \text{CCl}_2$ (~57%) $\rightarrow \text{NH}_2\text{CDCl}^+ (\text{NH}_2\text{CHCl}^+) + \text{HCl} (\text{DCl})$ (~43%)	7.8 ± 1.5
$(i\text{-C}_3\text{H}_7)_2\text{O}$	$+0.5^c$	$\text{CCl}_2\text{D}^+ + (i\text{-C}_3\text{H}_7)_2\text{O} \rightarrow \text{C}_3\text{H}_7^+ + i\text{-C}_3\text{H}_7\text{OC}_2\text{H}_5$	13.0 ± 3.0
$\text{C}_6\text{H}_5\text{NH}_2$	$+6.2^c$	$\text{CCl}_2\text{D}^+ + \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2\text{D}^+ + \text{CCl}_2$ (1%) $\rightarrow \text{C}_6\text{H}_5\text{NH}_2^+ + \text{CCl}_2\text{D}$ (99%)	10 ± 5

^a In units of $\text{cm}^3/(\text{molecule s})$. ^b Relative proton affinity derived from scales of ΔG° for various proton transfer reactions ($\text{AH}^+ + \text{B} \rightleftharpoons \text{BH}^+ + \text{A}$) at 300 K⁴ and 600 K;⁵ $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and $\Delta H^\circ = \text{PA}(\text{A}) - \text{PA}(\text{B})$. ^c Relative proton affinity derived from values of ΔG° reported in ref 4 and entropy changes estimated from considerations of symmetry and intramolecular interactions.⁶ ^d $\text{PA}(\text{NH}_3)$ cited in ref 5 is 202.3 ± 2 kcal/mol (taking $\Delta H_f(\text{H}^+) = 367.2$ kcal/mol). Corrections to this value necessitated by revisions of the heats of formation of standard bases and measurements of entropy changes for proton-transfer reactions⁷ and the use of a value of 365.2 kcal/mol for $\Delta H_f(\text{H}^+)$ ⁹ lead to $\text{PA}(\text{NH}_3) = 207.3 \pm 2$ kcal/mol.

As noted before, CCl_2D^+ reacts with CH_3OCH_3 exclusively via a hydride-transfer reaction. Hydride transfer also occurs in the reaction with $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$. However, deuteron transfer from CCl_2D^+ is also observed as a minor channel; the occurrence of this reaction was not discerned in our earlier experiments because deuteration was not used, and the product from the relatively minor reaction with CCl_2H^+ was obscured by the presence of a large abundance of $(\text{C}_2\text{H}_5)_2\text{OH}^+$ from other reactions. The observation of this deuteron-transfer reaction means that the proton affinity of CCl_2 is actually lower than our previous estimate by at least 4.8 kcal/mol.

In contrast, in the case of $(n\text{-Pr})_2\text{O}$ and $(i\text{-Pr})_2\text{O}$, no deuteron transfer from CCl_2D^+ was observed, even though the proton affinities of these molecules lie, respectively, 1.6 and 5.3 kcal/mol above that of diethyl ether. Instead, a fast displacement reaction was observed in both cases:



In the case of the $\text{CCl}_2\text{D}^+ - (\text{CH}_3)_2\text{S}$ reaction, we confirmed our earlier observation that proton transfer does not occur, even though $\text{PA}(\text{CH}_3\text{SCH}_3) \approx \text{PA}(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5)$. In this case, the competing hydride-transfer reaction is seen to be favorable. For methyl ethyl sulfide, hydride transfer is also the exclusive reaction channel.

The predominant reaction of CCl_2D^+ with aniline is charge transfer, although a small amount (~1%) of deuteron transfer was observed. The charge-transfer reaction is 17 kcal/mol exothermic,⁹ in our previous investigation of this subject,² as well as other work from this laboratory,¹⁰ it has been noted that exothermic charge-transfer reactions generally predominate over competing reaction channels even if the alternate channels are more exothermic. In this case, the proton-transfer channel is less exothermic ($\Delta H_{\text{PT}} \approx -14$ kcal/mol) than the charge transfer and would not be expected to compete.

There are several factors contributing to uncertainty in the derivation of a value of $\Delta H_f(\text{CCl}_2)$ from these results. These include (1) the near impossibility of pinpointing from such experiments (in which other fast reactions compete with proton transfer) the energy at which proton (deuteron) transfer from CCl_2H^+ (CCl_2D^+) is thermoneutral; (2) the difficulties associated with the assignment of absolute values to the proton affinity scale, and (3) the uncertainties in the heat of formation of CCl_2H^+ (CCl_2D^+). However, the results given in Table I indicate that $\text{PA}(\text{CCl}_2) < \text{PA}(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5)$. Accepting a value of 207.3 ± 2 kcal/mol for $\text{PA}(\text{NH}_3)$ (Table I, footnote d), this leads to an estimate of $\text{PA}(\text{CCl}_2) \leq 202.5 \pm 2$ kcal/

mol. Taking a value of 211 kcal/mol for $\Delta H_f(\text{CCl}_2\text{H}^+)$,¹¹ and 365.2 kcal/mol for $\Delta H_f(\text{H}^+)$,⁹ one obtains $\Delta H_f(\text{CCl}_2) \leq 47.8 \pm 2$ kcal/mol. Values in the literature for $\Delta H_f(\text{CCl}_2)$ range from 57¹² to 40 kcal/mol.^{13,14}

References and Notes

- B. A. Levi, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 8454 (1977).
- S. G. Lias and P. Ausloos, *Int. J. Mass Spectrom. Ion Phys.*, **22**, 135 (1976).
- (a) J. R. Eyler, P. Ausloos, and S. G. Lias, *J. Am. Chem. Soc.*, **96**, 3673 (1973). (b) P. Ausloos, S. G. Lias, and J. R. Eyler, *Int. J. Mass Spectrom. Ion Phys.*, **18**, 261 (1975). (c) J. Vogt and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 6682 (1975). (d) J. L. Beauchamp in "Interactions Between Ions and Molecules", P. Ausloos, Ed., Plenum Press, New York, N.Y., 1975, p 413.
- (a) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977); (b) R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Wiley-Halsted, New York, N.Y., 1975, p 31.
- R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976).
- S. G. Lias and P. Ausloos, *J. Am. Chem. Soc.*, **99**, 4831 (1977).
- P. Ausloos and S. G. Lias, *J. Am. Chem. Soc.*, **100**, 1953 (1978).
- Reactions analogous to eq 3 are also observed for $\text{CCl}_2\text{H}^+ - \text{AsH}_3$ and $\text{CCl}_2\text{H}^+ - \text{PH}_3$ reaction pairs (P. Ausloos and S. G. Lias, unpublished results).
- H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl.*, **1**, 6 (1977).
- P. Ausloos and S. G. Lias, *Int. J. Chem. Kinet.*, in press.
- (a) F. P. Lossing, *Bull. Soc. Chim. Belg.*, **81**, 125 (1972); (b) A. S. Werner, B. P. Tsai, and T. Baer, *J. Chem. Phys.*, **60**, 3650 (1974).
- D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., No. 37*, JANAF Thermochemical Tables (1971).
- S. W. Benson and H. E. O'Neil, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., No. 21*, "Kinetic Data on Gas Phase Unimolecular Reactions" (1970).
- A more recent private communication from S. W. Benson (Sept 10, 1975) indicates that a value of 47 ± 3 kcal/mol is favored. (This was the value cited in ref 2.)

P. Ausloos,* S. G. Lias

National Bureau of Standards
Washington, D.C. 20234

Received January 25, 1978

Homogeneous Catalysis of the Water Gas Shift Reaction by Mixed-Metal (Iron/Ruthenium) Catalysts

Sir:

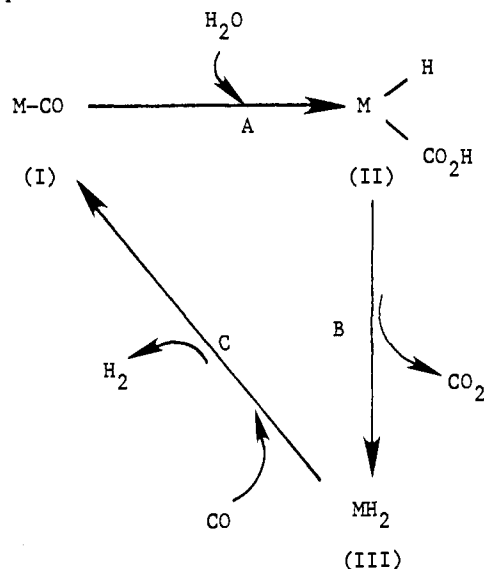
The water gas shift reaction (eq 1) is an important pathway for the formation of dihydrogen from water using the reducing equivalents of carbon monoxide. Production of H_2 via the shift reaction is a process certain to have increasing significance given the need to derive a larger fraction of energy require-

Table I. Activities of Various Metal Carbonyl Catalysts for the Water Gas Shift Reaction in Alkaline Aqueous Ethoxyethanol Solution^a

Initial complex ^b	Activity ^c
Ir ₄ (CO) ₁₂	5.3
H ₂ Ru ₄ (CO) ₁₃	4.4
H ₄ Ru ₄ (CO) ₁₂	3.7
Ru ₃ (CO) ₁₂	2.8 ^d
Fe(CO) ₅	1.0
Rh ₆ (CO) ₁₆	3.4 ^e
Ru ₆ C(CO) ₁₇	1.5
H ₃ Re ₃ (CO) ₁₂	0.15
Re ₂ (CO) ₁₀	0.1
H ₂ FeRu ₃ (CO) ₁₃	10.3

^a $T = 100\text{ }^\circ\text{C}$, $P_{\text{CO}} = 0.9\text{ atm}$; reaction carried out in all-glass vessels, stirred magnetically. ^b Solution prepared from 0.04 mmol of complex, 2 mmol of KOH, 0.02 mol of H₂O, and 3 mL of ethoxyethanol. ^c Moles of H₂ per mole of complex per day as determined by calibrated, temperature-programmed GC analysis. ^d This activity is about double that reported earlier¹ for somewhat different reaction conditions. However, the activity differences can be largely attributed to calibration errors in the earlier gas chromatographic analyses. ^e May be heterogeneous.

Scheme I



ments from coal reserves. Earlier we reported¹ a homogeneous catalyst for this reaction prepared from ruthenium carbonyl, Ru₃(CO)₁₂, in alkaline aqueous ethoxyethanol solution which is active under relative mild conditions ($T = 100\text{ }^\circ\text{C}$, $P_{\text{CO}} = 0.9\text{ atm}$). Continuing work in this laboratory has now demonstrated both that a number of other metal carbonyl complexes are active under analogous conditions and that ruthenium carbonyl forms active catalysts in a wide variety of reaction media, including acidic solutions. Lastly, a particularly interesting discovery is that mixed ruthenium/iron carbonyl catalysts are considerably more active in basic solutions than either of these metal carbonyls alone.

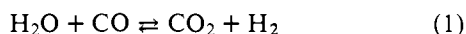


Table I summarizes the activities of different catalyst solutions prepared from various metal carbonyl complexes in alkaline aqueous ethoxyethanol solution ($T = 100\text{ }^\circ\text{C}$, $P_{\text{CO}} = 0.9\text{ atm}$). In each case (including Re₂(CO)₁₀), the reactions were followed over periods of days to demonstrate the catalytic nature of the system with respect to the metal complex. The stoichiometries (CO₂ and H₂ produced vs. CO consumed) generally correspond to eq 1 within the uncertainties of the GC

Table II. Catalysis by Ruthenium Carbonyl, by Iron Carbonyl, and by Iron/Ruthenium Carbonyl Mixtures in Various Media ($T = 100\text{ }^\circ\text{C}$, $P_{\text{CO}} = 0.9\text{ atm}$)

Complex ^a	Reaction medium	Activity ^b
Ru ₃ (CO) ₁₂	KOH/ethoxyethanol ^c	2.8 (0.9)
Fe(CO) ₅	KOH/ethoxyethanol ^c	1.0 (1.0)
Ru ₃ (CO) ₁₂ /Fe(CO) ₅ ^d	KOH/ethoxyethanol ^c	7.4 (4.2)
H ₄ Ru ₄ (CO) ₁₂	Piperidine/ethoxyethanol ^e	8.0 (2.0)
Fe(CO) ₅	Piperidine/ethoxyethanol ^e	0.9 (0.9) ^f
H ₄ Ru ₄ (CO) ₁₂ /Fe(CO) ₅	Piperidine/ethoxyethanol ^e	30.0 (12.0)
H ₄ Ru ₄ (CO) ₁₂	Pyridine ^g	13.2 (3.3)
Fe(CO) ₅	Pyridine ^g	~1-3 (~1-3) ^h
H ₄ Ru ₄ (CO) ₁₂ /Fe(CO) ₅	Pyridine ^g	~12-30 (5-12) ^h
H ₄ Ru ₄ (CO) ₁₂	H ₂ SO ₄ /ethoxyethanol ⁱ	~18 (4.5)
H ₄ Ru ₄ (CO) ₁₂	H ₂ SO ₄ /diglyme ^j	31.6 (7.9)
Ru ₃ (CO) ₁₂	H ₂ SO ₄ /diglyme ^j	33.3 (11.1)
Fe(CO) ₅	H ₂ SO ₄ /diglyme ^j	0.0 (0.0)
Ru ₃ (CO) ₁₂ /Fe(CO) ₅	H ₂ SO ₄ /diglyme ^j	14.8 (7.4)

^a Except where noted, 0.04 mmol of each complex listed was added to the solution. ^b Moles of H₂ per day per mole of complex (moles of Ru₃(CO)₁₂ or H₄Ru₄(CO)₁₂ plus moles of Fe(CO)₅). Values in parentheses are normalized activities: moles of H₂ per day per gram-atom of metal added initially to the system. ^c 2 mmol of KOH, 0.02 mol of H₂O, 3.0 mL of ethoxyethanol. ^d 0.04 mmol of Ru₃(CO)₁₂/0.064 mmol of Fe(CO)₅. ^e 1.5 mL of piperidine, 2.8 mL of ethoxyethanol, 0.02 mol of H₂O. ^f Low CO₂/H₂ ratios. ^g 3.0 mL of pyridine, 0.02 mol of H₂O. ^h Reproducibility of this system was poor, a possible indication of heterogeneity. ⁱ 0.18 mmol of H₂SO₄, 0.02 mol of H₂O, 3.0 mL of ethoxyethanol. Activity decreased markedly after several days owing to the sublimation of Ru₃(CO)₁₂ out of the solution. ^j 1.8 mmol of H₂SO₄, 0.02 mol of H₂O, 3.0 mL of diglyme.

analysis techniques.¹ Also, tests in pressurized bombs (50 atm of CO) at higher temperature (135 °C) show Os₃(CO)₁₂ and [Ir(CO)₃Cl]₂ to form active catalysts, although these are less active than the Ru₃(CO)₁₂ based system under the same conditions. Thus, catalytic activity for the shift reaction appears to be a rather general property of the metal carbonyls in alkaline solution.²⁻⁴

The similarity of the catalysts based on Ru₃(CO)₁₂, on H₂Ru₄(CO)₁₃, or on H₄Ru₄(CO)₁₂ as the initially added complex is not surprising. The ¹H NMR and IR spectra of the catalyst mixtures indicate that the principal ruthenium species in each solution is the well-characterized H₃Ru₄(CO)₁₂⁻ anion.⁵ Another hydride resonance is seen in the ¹H NMR spectra of these solutions, and, since H₂SO₄ neutralization gives significant quantities of H₂Ru₄(CO)₁₃,⁶ as well as H₄Ru₄(CO)₁₂ and Ru₃(CO)₁₂, the presence of HRu₄(CO)₁₃⁻ in the catalyst solutions is implicated. Scheme I depicts a hypothetical cyclic mechanism composed of steps each having well-characterized, published analogues.⁷ In the ruthenium solutions, a logical proposition would be for this cycle to be operating with HRu₄(CO)₁₃⁻ (or H₂Ru₄(CO)₁₃) as species I and H₃Ru₄(CO)₁₂⁻ (or H₄Ru₄(CO)₁₂) as species III.

Step C in Scheme I involves reductive elimination of H₂ and addition of CO. A logical mechanism for metal complexes would be the reductive elimination followed by CO addition to the coordinatively unsaturated complex. However, preliminary rate studies with the alkaline solution, ruthenium based catalyst, indicate a first-order rate dependence on P_{CO}. Since CO addition to an unsaturated complex seems an unlikely rate-limiting step for this cycle, one is led to speculate that CO is in fact participating in a rate-limiting dihydrogen elimination pathway.

The most striking feature of Table I is the high activity of the catalyst prepared from the mixed metal cluster $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$. Similarly, mixtures of $\text{Fe}(\text{CO})_5$ and $\text{Ru}_3(\text{CO})_{12}$ form catalysts in alkaline solution considerably more active than either metal carbonyl individually (Table II). Spectral characterization as well as isolation of various reaction components indicate the presence of several mixed-metal clusters including $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ in these solutions. The source of the synergetic behavior of the iron/ruthenium mixtures is uncertain. However, the key may lie with the stabilities of the mixed-metal hydridocarbonyl clusters toward reductive elimination of dihydrogen. For example, $\text{H}_4\text{FeRu}_3(\text{CO})_{12}$ is reportedly⁸ less stable toward loss of H_2 than is $\text{H}_4\text{Ru}_4(\text{CO})_{12}$; thus, if reductive elimination were rate limiting, this difference could have a marked effect on the relative catalytic activities. We are investigating this hypothesis with kinetics studies of H_2 elimination from several of these complexes and the role of CO in this reaction.

Ruthenium carbonyl forms active catalysts in other reaction media including aqueous piperidine/ethoxyethanol, aqueous pyridine, and acidic aqueous diglyme solutions⁹ (Table II) and, according to a recent report,¹⁰ in aqueous trimethylamine/tetrahydrofuran. Notably, marked enhancement of activity is again seen for the mixed Fe/Ru catalysts in the piperidine and pyridine solutions but not in the acidic diglyme solutions.

The greater activities of the ruthenium and Fe/Ru amine solutions compared with alkali base solutions may be the result of several perturbations. One possibility is that the amines are participating in direct attack on coordinated carbonyl, as previously reported¹¹ for $\text{Fe}(\text{CO})_5$, thus accelerating the activation step (step A in Scheme I). However, solvent effects alone may play a major role given that the amine concentrations are sufficient to change markedly the medium properties. Such effects on a rate-determining step or key equilibrium in a cycle such as Scheme I would have major consequences on the catalytic activity.

The high activity of the ruthenium catalysts in acidic solution may be simply the result of shifts in pH dependent equilibria. The key steps in Scheme I are likely to be activation of CO by nucleophilic attack on M-CO and reductive elimination of H_2 from MH_2 . If M-CO is either $\text{HRu}_4(\text{CO})_{13}^-$ or $\text{H}_2\text{Ru}_4(\text{CO})_{13}$, the latter species (which is favored by lowering the pH) should be the more susceptible to nucleophilic attack by H_2O or OH^- . We have demonstrated that after the first day the alkaline catalyst solutions prepared with KOH are ca. pH 10; thus H_2O (6 M) is probably the important nucleophile under this condition and at lower pH. In addition it is likely that $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ is more reactive toward reductive elimination than is the deprotonated analogue $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$. The failure of the mixed-metal system to show enhanced activity in acidic solution is unexplained; however, qualitative comparison of the reaction solutions (color, IR spectra, etc.) show, as expected, these systems to have considerably different characters in the acidic and basic media. These are mechanistic aspects of the various catalysts under further study in these laboratories.

Acknowledgments. This work was supported by the Department of Energy, Office of Basic Energy Sciences. Howard Walker and Professor Ralph G. Pearson contributed significantly to the discussion and interpretation of these results.

References and Notes

- (1) R. M. Laine, R. G. Rinker, and P. C. Ford, *J. Am. Chem. Soc.*, **99**, 252 (1977).
- (2) This view is reinforced by the recent unpublished reports that $\text{Cr}(\text{CO})_6$,³ $\text{Mo}(\text{CO})_6$,⁴ and $\text{W}(\text{CO})_6$ ⁴ may also form shift reaction catalysts in alkaline solution. The conditions of these studies were very different from those reported here and comparison of activity cannot be objectively made.
- (3) D. J. Darensbourg, M. Y. Darensbourg, R. R. Burch, Jr., and J. A. Froelich,

reported as the American Chemical Society Inorganic Chemistry Symposium, Athens, Ga., Feb 1978.

- (4) C. C. Frazier, R. Hanes, A. D. King, Jr., and R. B. King, reported at the same symposium.³
- (5) (a) J. W. Koepke, J. R. Johnson, S. A. R. Knox, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3947 (1975). (b) The ^1H NMR spectra were recorded under a CO atmosphere at normal probe temperature, $\sim 30^\circ\text{C}$. Under these conditions the species in solution underwent no changes detectable by their IR spectra over a period of 24 h.
- (6) B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. H. Robinson, *J. Chem. Soc. A*, 3461 (1968).
- (7) (a) A. C. Harkness and J. Halpern, *J. Am. Chem. Soc.*, **83**, 1258 (1961); (b) E. L. Meutteries, *Inorg. Chem.*, **4**, 1841 (1965); (c) D. J. Darensbourg and J. A. Froelich, *J. Am. Chem. Soc.*, **99**, 5940 (1977); (d) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 443 (1969); (e) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Am. Chem. Soc.*, **91**, 1346 (1969).
- (8) S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3942 (1975).
- (9) Eisenberg recently reported (C. H. Cheng, D. E. Hendricksen, and R. Eisenberg, *J. Am. Chem. Soc.*, **99**, 2791 (1977)) that a rhodium carbonyl species $[\text{Rh}(\text{CO})_2]_2$ forms an active catalyst for the shift reaction in an acidic aqueous solution containing HCl, NaI, and acetic acid.
- (10) H. C. Kang, C. H. Mauldin, T. Cole, W. Stegair, K. Cann, and R. Pettit, *J. Am. Chem. Soc.*, **99**, 8324 (1977).
- (11) W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer, and N. Korzumi, *J. Am. Chem. Soc.*, **87**, 3080 (1965).
- (12) Department of Chemistry.
- (13) Department of Chemical and Nuclear Engineering.

Peter C. Ford,*¹² Robert G. Rinker¹³
Charles Ungermann, Richard M. Laine
Vincent Landis, Sergio A. Moya

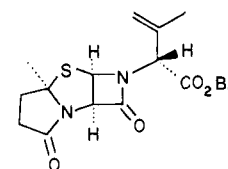
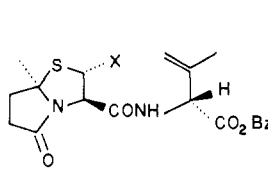
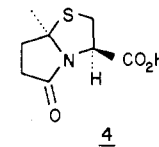
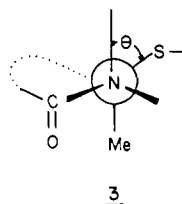
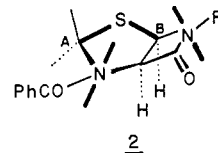
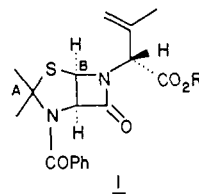
Department of Chemistry and
Department of Chemical and Nuclear Engineering
University of California, Santa Barbara, California 93106

Received March 8, 1978

Stereospecific Synthesis of Penicillins. Stereochemical Control in the Conversion of a Peptide into a Penicillin

Sir:

Recently we described the stereospecific total synthesis of a penicillin from a dipeptide,¹ in which the thiazolidine β -lactam **1**² was converted via a seven-step sequence into a penicillin. This lengthy sequence resulted from the intrinsically



- 5** a : X = H
 b : X = OCOPh
 c : X = Cl