460 ± 30 (calcd 420).

(13) The major products are $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ and a new organozirconium complex tentatively assigned the empirical formula $\{(\eta^5\text{-}C_5Me_5)[C_5\text{-}(CH_3)_3(CH_2)_2]Zr\}_n$ (NMR).

(14) (a) Unfortunately, 2-methylpropane suffers severe fragmentation upon ionization even at low energies, loss of CH_3 being the primary process. Comparison of the relative intensities of the parent ion and the next two lower mass ions gave fairly reliable results; however, supplementation of these mass spectral data with infrared spectra was necessary. The characteristic IR bands used were as follows. **2a:** $\delta(CH_3)$ 1480, 1380, 1335 cm⁻¹; $\nu(C–C)$ 1180 cm⁻¹. **2b:** $\nu(C–D)$ 2145 cm⁻¹; $\delta(CH_3)$ 1475, 1380 cm⁻¹; $\nu(C–C)$ 1235, 1225 cm⁻¹. **2c:** $\nu(C–D)$ 2180, 2160 cm⁻¹; $\delta(CH_3)$ 1470, 1385 cm⁻¹; $\nu(C–C)$ 1295, 1220 cm⁻¹. **2d:** $\nu(C–D)$ 2165 cm⁻¹; $\delta(CH_3)$ 1470, 1385 cm⁻¹; $\nu(C–C)$ 1285, 1155 cm⁻¹. (b) According to Scheme I the observed ratio of $k(H)/k(D)$ is a composite of a kinetic deuterium isotope effect for **3 → 4** and a thermodynamic deuterium isotope effect for the fast pre-equilibrium step **1 ⇌ 3.**

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(19) Although β-H abstraction from the isobutyl group of intermediate **10** could conceivably lead to isobutylene and an ethyl hydride derivative, no evidence of this reaction is observed. We attribute the much greater preference for β-H abstraction from the ethyl group to steric factors which disfavor coordination of the bulky olefin isobutylene in the coordination of the sphere of the alkyl hydride (as would be required for generation of the ethyl hydride). This argument is supported by the observation that isobutylene does not promote reductive elimination of isobutane from **1**.⁹

(20) P. T. Wolczanski and J. E. Bercaw, manuscript in preparation.

(21) Gell and Schwartz have postulated that reaction of the closely related alkyl hydride complex, $(\eta^5\text{-}C_5H_5)_2Zr(H)(CH_2C_6H_{11})$, with H_2 proceeds via a fundamentally different mechanism involving hydride abstraction from H_2 by the formal Zr(IV) center.⁷ Elimination of methylcyclohexane is postulated to occur in a subsequent step by electrophilic attack of H^+ on the resulting five-coordinate intermediate. A faster, competitive attack of H^+ on this intermediate to regenerate H_2 was postulated to account for the observed incorporation of deuterium into the hydride position of the alkyl hydride upon exposure to D_2. We find no such exchange when **1a** is exposed to D_2. Thus treatment of a toluene solution of **1a** with a 5 M excess of D_2 (1 atm) at −15 °C for 3 min led to a 3:1 mixture of **1a** and $(\eta^5\text{-}C_5Me_5)_2Zr(H)_n(D)_{2-n}$ ($n = 0, 1,$ or 2). Analyses of the residual gas phase by mass spectrometry and the resulting mixture of the two organozirconium compounds by ¹H NMR indicated no detectable exchange of deuterium with the hydride position of residual **1a**.

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On the Existence of Colorless Europium(IV)

Sir:

Recently, Firor and Seff[1] presented crystallographic evidence for the novel oxidation state europium(IV) in zeolites. Obviously, it is interesting to determine the local symmetry, the coordination number N, and the preponderant electron configuration[2] defining the oxidation state in noncatenated transition-group (and other) atoms. However, here is a case where visible spectra can be used to render the conclusion highly improbable. First of all, it is well known[3,4] that the difference, 3.6 eV, between the ionization energies[1] of gaseous Eu^{3+} and Pr^{3+} for the greatest part is conserved in the standard oxidation potential, E^0, of Eu(III)/Eu(IV) and Pr(III)/Pr(IV) (estimated from the refined spin-pairing theory for the aqua ions, +6.4 and +3.4 V, respectively). This constitutes a major distinction from the other transition groups[2] where such differences can be highly attenuated. It is always conceivable that a new type of ligand may be found, such as the bidentate phosphine[5] stabilizing Fe(IV), Ni(IV), and Cu(III) by unexpectedly effective covalent bonding. However, it is excluded that $4f^5$ Eu(IV) could be *colorless*. Traces of Pr(IV) and

Tb(IV) in mixed oxides provide strong colors, such as purple ThO_2, chamois CeO_2 and orange Y_2O_3, and it can be easily extrapolated from the observed positions[6] of electron-transfer bands[7,8] that the strong transitions of Eu(IV) surrounded by oxygen-containing ligands would start in the far-infrared and probably would correspond to lower minimum energy of the potential surface[6] producing spontaneous redox reactions. It has previously been pointed out[9] that such strong colors might be a helpful indicator for ephemeral formation of quadrivalent intermediates (say, at low temperature) in solution. Though the positions of electron-transfer bands to a certain extent[6] depend on the distances to the ligating atoms, they are not exceedingly sensitive to changes of the coordination number, N, and, for instance, $M\{N[Si(CH_3)_3]_2\}_3$ having $N = 3$ shows the same colors[3] (orange for M = Eu and yellow for M = Yb) as $M[S_2CN(C_4H_9)_2]_4^-$ with $N = 8$.

A closer analysis of the crystallographic data[1] shows some similarity with the classical case[10] of $Cr(NH_3)_3(O_2)_2$ originally described as a chromium(II) superoxo complex (based on the intraligand oxygen–oxygen distance) but now recognized as Cr(IV) and peroxo ligands. A review of a large number of Eu(III)–oxygen internuclear distances[11] shows a remarkably large dispersion (e.g., 2.29 Å in EuOCl and six distances between 2.31 and 2.37 in Å $Eu(dpm)_3(py)_2$ with $N = 8$ compared with B-type Sm_2O_3 where the average Sm–O distance, 2.46 Å, is the mean value of lengths scattered from 2.25 to above 2.7 Å). It may be argued that the oxidized zeolite[1] has the low $N = 4$ predisposing to shorter distances. Anyhow, the values 2.28 and 2.13 ± 0.04 Å cannot prove the presence of Eu(IV). The situation is rather different in the product obtained by reaction with chlorine where the lower of the two Eu–Cl distances ($N = 5$), 2.06 and 2.31 Å, is exorbitantly shorter than 2.835 and 2.919 Å observed[11] in $EuCl_3$ ($N = 9$). Nevertheless, the lack of color strongly suggests an alternative explanation involving Eu(III).

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(12) On sabbatical leave of absence from Département de Chimie minérale, analytique et appliquée, Université de Genève, Switzerland.
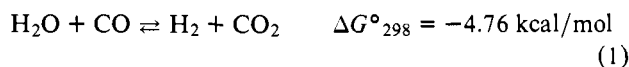
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Homogeneous Catalysis of the Water Gas Shift Reaction Using a Platinum Chloride–Tin Chloride System

Sir:

The water gas shift reaction

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad \Delta G°_{298} = -4.76 \text{ kcal/mol} \qquad (1)$$

Table I. Results of Catalytic Runs of the WGS Reaction Using the Platinum Chloride–Tin Chloride Homogeneous Catalyst

| run[a]	time, h	CO[b] (consumed)	H_2[b]	CO_2[b]	cycles/day
I	37	9.3	8.8	9.6	25.5
II[c]	38	8.9	9.0	9.2	24.4
III[d]	33	7.3	8.2	8.3	24.6
IV[e]	31	7.9	8.3	7.2	25.7

[a] [Pt] = ~4 mM and [Pt]:[Sn] = 1:30 in all runs under 400 Torr of CO pressure at 88 ± 2 °C. [b] In millimoles. [c] Initial [Pt]:[Sn(II)] ratio is 1:2. [d] Initial [Pt]:[Sn(II)] ratio is 1:4. [e] Recharge of run I.

finds industrial application in CO removal, H_2 production, and the adjustment of H_2:CO ratios in synthesis gas used for methanation, methanol synthesis, and other CO reduction chemistry.[1,2] While efforts to catalyze this reaction using metal complexes in solution can be traced back nearly half a century,[3] it is only in the past year that successful homogeneous catalyst systems for the water gas shift (WGS) reaction have been reported.[4-8] In the first such report, Ford and co-workers[4] showed that $Ru_3(CO)_{12}$ in basic ethoxyethanol catalyzes eq 1, while, more recently, Pettit et al.[6] have described the use of other noble metal clusters in THF/aqueous amine solutions as WGS catalysts. We have reported[5] an apparently more active catalyst for eq 1 based on aqueous acidic solutions of rhodium carbonyl iodide in which strictly mononuclear catalysis occurs.[9] In the present communication, we describe an entirely different WGS catalyst system which is not only more active than those previously reported, but which also incorporates in a novel way the Sn(II)/Sn(IV) redox couple in the observed catalysis.

The ability of CO to reduce Pt^{2+} to the metal with concomitant CO_2 production, the π-acceptor properties of $SnCl_3^-$ which inhibit a similar reduction by H_2,[10] and the observation of H_2 evolution from aqueous acetic acid solutions of Pt^{2+} containing HCl and excess $SnCl_2$ led us to examine the efficacy of platinum chloride–tin chloride systems in catalyzing the WGS reaction. An efficient catalyst for eq 1 was thus obtained, consisting of 0.1 g of K_2PtCl_4 (0.23 mmol) and 2.5 g of $SnCl_4 \cdot 5H_2O$ (7.1 mmol) dissolved in 40 mL of glacial acetic acid, 10 mL of concentrated HCl, and 10 mL of H_2O. Catalysis of eq 1 was established in the same manner as previously reported, except that CH_4 was used as the internal calibrant rather than N_2, thereby allowing the complete analysis to be done on a Poropak Q column. All runs were conducted at 88 (±2) °C under initial CO pressures of ~400 Torr measured at ambient room temperature. The results of several runs are presented in Table I, and product plots are shown in Figure 1. Runs I and IV employ the same catalyst solution, the latter being obtained after degassing the system and recharging with CO. In the other runs of Table I and those shown in Figure 1, the initial [Sn(II)]:[Pt] ratios are varied while maintaining a fixed [Sn_{total}]:[Pt] ratio.

The results of these runs clearly establish water gas shift catalysis. The stoichiometry of eq 1 is evidenced by the data given in Table I, and the rate of catalysis at 88 °C corresponds to ~25 turnovers/day per platinum ion with no loss of activity upon recharging. The system is thus several times more active than the previously reported rhodium carbonyl iodide catalyst.[5] Figure 1 shows that, although the different catalyst preparations yield different initial product distributions, they ultimately result in H_2 and CO_2 being produced in a 1:1 ratio. Moreover, once this occurs, the different preparations show the *same* rate of catalysis, suggesting convergence to a single catalyst system containing both Sn(II) and Sn(IV) species in a particular concentration ratio.[11]

Requirements and features of the catalyst were probed through experiments which can be summarized as follows: (i)
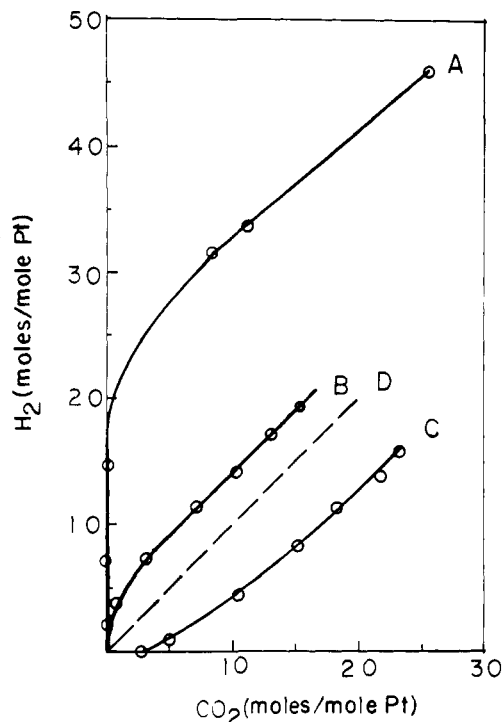

Figure 1. Product distribution for different initial [Sn(II)]:[Pt] ratios. Run A corresponds to an initial [Sn(II)]:[Pt] ratio of 30:1, run B to a ratio of 10:1, and run C to a ratio of 0:1. In all of these runs, the [Sn_{total}]:[Pt] ratio was held fixed at 30:1. The dashed line of unit slope corresponds to the product distribution for true WGS catalysis from the start of a run.

no reaction takes place in the absence of the platinum chloride salt; (ii) the omission of tin chlorides greatly decreases catalytic activity, leading to decomposition and formation of a brown precipitate; (iii) large excesses of tin chlorides inhibit catalysis—e.g., at a [Sn_{total}]:[Pt] ratio of 300:1, no WGS catalysis occurs;[12a] (iv) if acetic acid is replaced by H_2O, only a trace of CO_2 is produced and a dark brown precipitate is obtained; and (v) no catalysis occurs in the absence of either a strong protic acid or a chloride source as shown by independent variation of each component. It thus appears that platinum and tin chlorides in a given ratio range, a strong protic acid, Cl^-, and acetic acid solvent are essential components of the catalyst system. The interconversion of Sn(II) and Sn(IV) in the catalyst system was established in the following way. First, a catalyst preparation based on $SnCl_2 \cdot 2H_2O$ similar to that used in run A of Figure 1 was heated at 88 °C for 8 h, yielding ~1 molecule of H_2 per Sn(II) added. Addition of $Et_4N^+Cl^-$ under strictly anaerobic conditions led to precipitation of $(Et_4N)_2[SnCl_6]$, the identity of which was established by independent preparation and spectral and electrochemical properties. Because the reaction had been driven to completion by the removal of product H_2 after 7 h, no $(Et_4N)[SnCl_3]$ was observed.[12b] Thus, Sn(II) was converted into Sn(IV) with H_2 as the only other major product. The reduction of Sn(IV) to Sn(II) was readily evidenced in catalyst preparations based on $SnCl_4 \cdot 5H_2O$ by the color changes which are attributable to the formation of $SnCl_3^-$ complexes of Pt(II) (vide infra) which accompany initial CO_2 production as in run C of Figure 1.[12c]
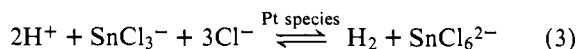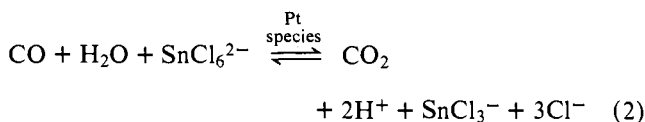
To determine the species present under catalytically active conditions, the catalysis was quenched by the addition of excess n-$Bu_4N^+Cl^-$ which yielded a precipitate containing ν_{CO} at 2055 and 2095 cm^{-1}. The former is due to the complex $[PtCl(CO)(SnCl_3)_2]^-$ reported previously by Kingston and Scollary,[13] while the latter is identified as belonging to the mono(trichlorotin) complex $[PtCl_2(CO)(SnCl_3)]^-$ which we have synthesized separately and analyzed.[14] When an isolated

Scheme I
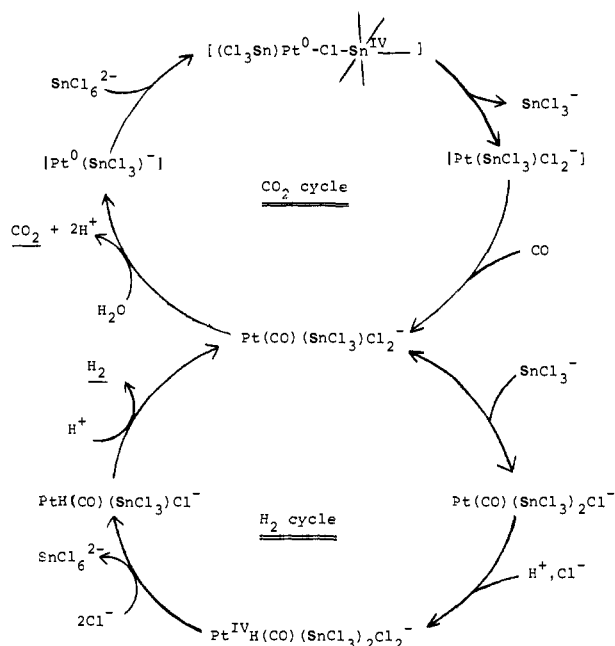
sample of the bis complex $[PtCl(CO)(SnCl_3)_2]^-$ was heated in the $HOAc/HCl/H_2O$ catalyst "solution" under N_2, hydrogen evolution was observed with little CO_2 being evolved. The mono complex $[PtCl_2(CO)(SnCl_3)]^-$ was isolated from this solution. In a separate experiment, dissolution of the mono complex in the catalyst "solution", followed by heating under CO, led within 10 min to CO_2 evolution corresponding to ~0.6 mol of CO_2 per Pt complex with only a trace of H_2 observed. In acetonitrile, $[PtCl_2(CO)(SnCl_3)]^-$ in the presence of $SnCl_4·5H_2O$ under CO reacted readily to form the bis complex. We conclude from these experiments that $[PtCl(CO)-(SnCl_3)_2]^-$ is most likely responsible in the catalysis for H_2 formation, that $[PtCl_2(CO)(SnCl_3)]^-$ is most likely responsible for CO_2 formation, and that the two complexes are related by either a stoichiometric reaction or a simple ligand substitution.

It is evident from the foregoing studies that the Sn(II)/Sn(IV) redox couple $(SnCl_6^{2-} + 2e \rightleftharpoons SnCl_3^- + 3Cl^-)$ is actively involved in the observed reaction chemistry, and hence in the mode of catalysis by this system. Through the intermediacy of the Sn(II)/Sn(IV) couple, the water gas shift reaction can be separated into two component reactions

$$CO + H_2O + SnCl_6^{2-} \overset{\text{Pt species}}{\rightleftharpoons} CO_2$$

$$+ 2H^+ + SnCl_3^- + 3Cl^- \quad (2)$$

$$2H^+ + SnCl_3^- + 3Cl^- \overset{\text{Pt species}}{\rightleftharpoons} H_2 + SnCl_6^{2-} \quad (3)$$

and a mechanism based on this separation can be proposed. This mechanism, which we describe as "coupled cycles", is shown in Scheme I. In the H_2-forming part of the catalysis, Sn(II) is oxidized to Sn(IV), while, in the oxidation of CO to CO_2, Sn(IV) is reduced back to Sn(II). The Sn(II)/Sn(IV) couple thus serves to shuttle electrons from CO to H^+ in this catalysis, each step of which occurs via the intermediacy of a platinum complex species.[15] The facts that at least one common platinum species exists for the two component reactions and that the tin product of one is a reactant for the other leads to a coupling of the component reactions such that, once the proper Sn(II):Sn(IV) ratio is attained, the stoichiometry of the shift reaction is followed in the observed catalysis.

With regard to the intimate formation of the product gases, it is probable that CO_2 forms via aqueous attack on a Pt(II)-coordinated carbonyl and that H_2 is produced via a platinum hydride species and its reaction with H^+.

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(11) (a) This [Sn(II)]:[Sn(IV)] ratio is not invariant throughout the catalysis, but changes as the partial pressures of CO, H_2, and CO_2 change in the course of each run. (b) A reviewer has suggested that significant solubility of CO_2 in the catalyst solution may alter the conclusions drawn from Figure 1. However, we find that CO_2 is not soluble to a significant extent in the reaction medium. Dissolution of small amounts of K_2CO_3 (1–3 mmol) into the catalyst preparation used for run A leads to quantitative evolution of CO_2, detected gas chromatographically.
(12) (a) The complex $[Pt(SnCl_3)_5]^{3-}$ can be isolated from these runs and in separate experiments has been shown to serve as a catalyst precursor for the present system. (b) In this experiment, the [Sn]:[Pt] ratio was 15:1. After heating for 7 h, 12.3 mol of H_2/mol of Pt had been released with no CO_2 formed. Removal of the H_2 and CO gases from above the solution, replacement by N_2, and further heating for 1 h led to an additional 3.2 mol of H_2/mol of Pt and a color change of the active catalyst solution from orange to pale yellow. Precipitation by the addition of $Et_4N^+Cl^-$ gave a colorless product which decomposed at 310 °C and showed $E_{1/2}$ at −1.57 V vs. $Ag/AgNO_3$ using differential pulse polarography and cyclic voltammetry. These values agree well with those from an independent preparation of the compound (I. Wharf and D. F. Shriver, *Inorg. Chem.*, **8**, 914 (1969)) and differ significantly from those for $(Et_4N)[SnCl_3]$ reported by Parshall (G. W. Parshall, *J. Am. Chem. Soc.*, **94**, 8716 (1972)). (c) In addition to the isolation experiments discussed below in the text, we have observed by visible–ultraviolet spectroscopy $[Pt(SnCl_3)_2Cl_2]^{2-}$ after the removal of CO from catalyst preparations based solely on Sn(IV).
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(14) The complex $[PtCl_2(CO)(SnCl_3)]^-$ exhibits two ν_{CO} values at 2095 and 2065 cm^{-1} which may be due to different geometric isomers. The 2095-cm^{-1} band is much more intense in the initially prepared sample, but, if a solution of the complex is allowed to stand, the 2065-cm^{-1} band becomes stronger at the expense of the higher energy ν_{CO}.
(15) The exact nature of the Pt species at each point in Scheme I is unknown, but it is highly probable that the intermediates are trichlorostannyl species. Except where indicated, the Pt oxidation state is assumed to be 2+. However, the active involvement of the Sn(II)/Sn(IV) couple via the platinum species requires at least transitory formation of Pt(0) and Pt(IV) species.

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Metallocenes: First Models for Nuclear Magnetic Resonance Isotope Shifts in Paramagnetic Molecules[1]

Sir:

The effect of isotopic substitution on NMR spectra of diamagnetic molecules has been widely studied[2] and this has led to numerous applications for the elucidation of structural and bonding parameters. It was an open question of general in-