Table I. Comparison of Fluorinated Products Obtained with NF_3O, COF_2, or SOF_2 with a Common Substrate

reactant (2 mmol)	products (% yield) for reaction with		
	NF_3O[a]	COF_2[b,c]	SOF_2[b,d]
$(C_6H_5)_3P$	$(C_6H_5)_3PF_2$ (80)	$(C_6H_5)_3PF_2$ (68)	$(C_6H_5)_3PF_2$ (44), $(C_6H_5)_3P{=}S$
$(CH_3)_3P$	$(CH_3)_3PF_2$ (60)	$(CH_3)_3PF_2$ (72)	$(CH_3)_3PF_2$ (25)
$(CH_3O)_3P$	$(CH_3O)_2P(O)F$ (~80) CH_3F (~60)		
$(C_2H_5O)_3P$	$(C_2H_5O)_2P(O)F$ (~50) C_2H_5F (~40)	$(C_2H_5O)_3PF_2$ (72)	$(C_2H_5O)_3PF_2$ (25)
$(n\text{-}C_4H_9O)_3P$	$(n\text{-}C_4H_9O)_2P(O)F$ (70) $n\text{-}C_4H_9F$ (~25)	$(n\text{-}C_4H_9O)_3PF_2$ (70)	$(n\text{-}C_4H_9O)_3PF_2$ (22)
$(C_2H_5O)_2P(O)H$	$(C_2H_5O)_2P(O)F$ (~100)	$(C_2H_5O)_2P(O)F$ (65)	$(C_2H_5O)_2P(O)F$ (~100)
$(n\text{-}C_4H_9O)_2P(O)H$	$(n\text{-}C_4H_9O)_2P(O)F$ (70)	$(n\text{-}C_4H_9O)_2P(O)F$ (60)	$(n\text{-}C_4H_9O)_2P(O)F$ (60)
$Ph_2PCH_2PPh_2$	$Ph_2PF_2CH_2PF_2Ph_2$ (75)		
$Ph_2PCH_2CH_2Ph_2$	$Ph_2PF_2CH_2CH_2PF_2Ph_2$ (75)	$Ph_2PF_2CH_2CH_2PF_2Ph_2$ (80)	
metal oxides	NR[e] at 200 °C, 24 h	metal fluorides and oxyfluorides	

[a] 100 °C, 2–4 h. [b] 25 °C, 10 h. [c] References 1 and 2. [d] Reference 3. [e] NR = no reaction.

Table II. Fluorination of Elements with NF_3O

element	product (% yield)	element	product (% yield)
Zn[a]	ZnF_2 (>99)	Pb[b]	PbF_2 (60)
Cd[a]	CdF_2 (>99)	As[d]	AsF_5 (90)
B[c]	BF_3 (80)	Sb[d]	SbF_5 (90)
Ga[a]	GaF_3 (>99)	Bi[e]	BiF_3 (>99)
Ge[a]	GeF_4 (75)	Fe[f]	NR[g]
Sn[c]	SnF_4 (>99)	Rh[f]	NR[g]
Se[a]	SeF_4/SeF_6 (80 combined)		

[a] 180 °C, 16 h. [b] 190 °C, 20 h. [c] 200 °C, 24 h. [d] 210 °C, 24 h. [e] 220 °C, 36 h. [f] 220 °C, 70 h. [g] No reaction.

>NC(O)F- and >NS(O)F-containing compounds were prepared, respectively.

$$>NH + NF_3O \xrightarrow{0\ °C} >NF + >NNO + \text{salt}$$

$$>NH + COF_2 \xrightarrow[CH_2Cl_2]{Et_3N} >NC(O)F + Et_3N{\cdot}HF$$

$$>NH + SOF_2 \xrightarrow[CH_2Cl_2]{Et_3N} >NS(O)F + Et_3N{\cdot}HF$$

Only $(CH_3)_2NH$ was found to form $(CH_3)_2NF$ when reacted with COF_2.[3] In the case of the nitrogen–hydrogen bond, the behavior of NF_3O is in sharp contrast to that of COF_2 and SOF_2 with similar systems.

Compounds with active C–H bonds, such as $(C_6H_5)_3CH$, CF_3CF_2H, and $CF_3C{\equiv}CH$ did not react with NF_3O under various conditions. That is, no reaction occurred between $(C_6H_5)_3CH$ and NF_3O at 0 or 25 °C for 12 h, between CF_3CF_2H and NF_3O at 0 or 25 °C in the presence of aqueous KOH, or between $CF_3C{\equiv}CH$ and NF_3O at 0, 25, or 80 °C. With these or similar systems, abstraction of hydrogen from tertiary carbon was observed in the case of COF_2 and SOF_2.

Trifluoroamine oxide was reacted with a variety of free elements at ~200 °C for 24 h

$$M + nNF_3O \xrightarrow{100\text{–}220\ °C} MF_y$$

$$M = As, Sb, Bi, Ge, Sn, Pb, B, Ga, Zn, Cd, Se$$

with 95–100% conversion in nearly every case (Table II). Only the binary fluorides were characterized.

The oxides of these elements were also exposed to NF_3O at 200–220 °C for ~24 h, but in all cases, only the unreacted starting materials were recovered. Interestingly, in contrast with the behavior of NF_3O toward free elements, COF_2 and SOF_2 did not react at all, but they could be reacted with metal oxides to form the corresponding fluorides.

Experimental Section

Caution! Trifluoroamine oxide is a strong oxidizer. Mixtures with both inorganic and organic materials are potentially explosive. Attempts to scaleup the synthetic methods presented in this paper should be avoided. Proper safety precautions should be taken when reacting trifluoroamine oxide with any substrate.

General Procedures. A conventional Pyrex glass vacuum system equipped with a Heise Bourdon tube gauge was used to handle gases and volatile liquids. Most of the starting materials and products were measured quantitatively by using *PVT* techniques. Volatile products were purified by fractional condensation (trap-to-trap distillation) and, when necessary, bulb-to-bulb distillation (Kugelrohr). ^{19}F NMR spectra were obtained on either a JEOL FX-90FT or a Varian EM360 NMR spectrometer with CCl_3F as an internal reference. Chemical shifts upfield of the reference are assigned negative values. Mass spectra were recorded with a VG 7070HS mass spectrometer operating at 10 eV.

Materials. Trifluoroamine oxide (Allied) was passed through two traps cooled at −78 °C to remove NO_2. Starting materials were obtained and treated as follows: $(C_2H_5O)_3P$, $(CH_3O)_3P$, and $(n\text{-}C_4H_9O)_3P$ (Aldrich) were distilled over $PbCO_3$ before use; $(CH_3)_3P$ (Strem), $(C_6H_5)_3P$ (Aldrich), $Ph_2PCH_2PPh_2$ (Strem), and $Ph_2PCH_2CH_2PPh_2$ (Strem) were used as received. The powdered elements As, Sb, Bi, Ge, Sn, Pb, B, Ga, Zn, Cd, and Se were used as received.

Reaction of Elements with NF_3O. A stainless-steel or Monel Hoke cylinder fitted with a stainless-steel or Monel Whitey valve was loaded with a known amount (~2 mmol) of the dry powdered element. A slight excess over the stoichiometric amount of NF_3O required was condensed into the cylinder at −196 °C by using standard vacuum-line techniques. The mixture was heated at 180–200 °C for 24 h. The progress of the reaction was checked by recording the IR spectrum of any volatile materials, including NF_3O. The formation of the fluoride products was confirmed by comparison of infrared and ^{19}F NMR spectral data with literature values.

Reaction of Phosphines and Phosphites with NF_3O. A 75-mL Monel Hoke cylinder fitted with a stainless-steel or Monel Whitey valve was charged with a known amount of compound (2–3 mmol) and cooled to −196 °C and evacuated. A slight excess over the stoichiometric amount of NF_3O required was condensed into the cylinder by standard vacuum-line techniques. A check was done for the completion of the reaction by following the IR spectrum of NF_3O. Trap-to-trap distillation or bulb-to-bulb distillation (Kugelrohr) was employed as necessary. The products were confirmed by comparison of infrared spectra, ^{19}F NMR spectra, and ^{31}P NMR spectral data with literature values.

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A Newly Proposed Cycle for the Water Gas Shift Reaction Homogeneously Catalyzed by Platinum and Tin Chloride

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A mechanism for catalysis of the water gas shift (WGS) reaction ($H_2O + CO = H_2 + CO_2$) by K_2PtCl_4 and $SnCl_4$ in a mixture of acetic and hydrochloric acids[1] has been described in

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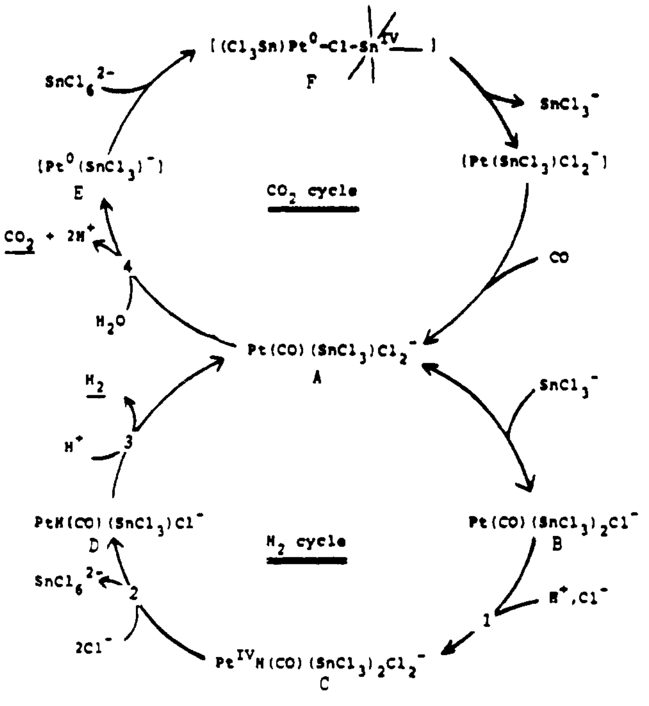

Figure 1. Coupled-cycle mechanism for the Pt–Sn-catalyzed water gas shift reaction according to ref 1.

several recent reviews.[2] The novel WGS catalytic system of Cheng and Eisenberg is more active than other previously reported systems and was claimed to involve the Sn(II)/Sn(IV) and Pt(0)/Pt(II)/Pt(IV) couples.[1] Careful control studies by Cheng and Eisenberg showed that with a high ratio of concentrations of Sn(II)/Sn(IV) more hydrogen than carbon dioxide was initially formed and at a low ratio of concentrations of Sn(II)/Sn(IV) more carbon dioxide than hydrogen was initially formed, but as the reaction proceeded, the catalytic stoichiometric 1/1 ratio of products was achieved. We present here an alternative interpretation of the data which is more in accord with studies of related systems that have appeared after the work of Cheng and Eisenberg.

It is important to note that Tolman catalytic cycles[3] are used to explain and evaluate reactions that are homogeneously catalyzed by transition-metal compounds in terms of stepwise reactions such as ligand substitution, oxidative addition, reductive elimination, electrophilic or nucleophilic attack on coordinated ligands, or migration.[4] Each reaction in the cycle should be consistent with experiments in closely related systems.[3] The intermediates in the cycle do not have to be isolated or spectroscopically detected, but the composition and structure should be consistent with studies of related systems. While Halpern has demonstrated that species which are isolated or spectroscopically detected may or may not be relevant to a catalytic cycle,[5] Tolman cycles are useful for explaining experimental results and designing systems for homogeneous catalysis.

I propose to revise the catalytic cycle for the WGS reaction catalyzed by K_2PtCl_4 and $SnCl_4$ that is shown in Figure 1 for the following reasons. Carbon dioxide has been proposed to be formed in the Pt(0)–Pt(II) cycle and hydrogen in the Pt(II)–Pt(IV) cycle. To maintain the stoichiometry of the WGS reaction ($H_2O + CO = H_2 + CO_2$), the two cycles must have the same turnover rate.

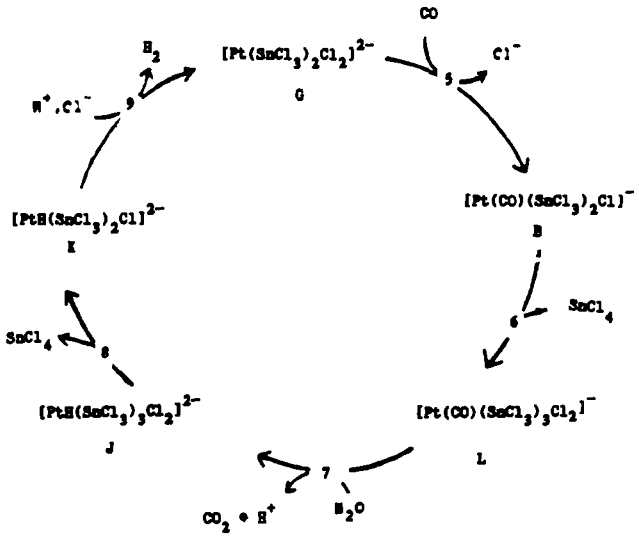

Figure 2. Newly proposed cycle for the Pt–Sn-catalyzed water gas shift reaction.

It is highly unlikely that the slowest (rate determining) reaction in the Pt(0)–Pt(II) cycle proceeds at the same rate as the slowest reaction in the Pt(II)–Pt(IV) cycle. The proposed decarboxylation of the anionic Pt(II) complex $[Pt(CO)(SnCl_3)Cl_2]^-$ (A) by reaction 4 rather than the decarboxylation of the Pt(IV) complex $[PtH(CO)(SnCl_3)_2Cl_2]^-$ (C) is not in accord with more recent studies[6] which have convincingly demonstrated that CO must be significantly activated by coordination to a metal in a cationic complex or high oxidation state in order to be susceptible to nucleophilic attack by water in acidic solutions. Activation of CO coordinated to Pt(II)[6c] and Rh(III)[7] for nucleophilic attack has been shown to be significantly inhibited in acidic solution. The observation that $[Pt(CO)(SnCl_3)_2Cl]^-$ (B) gives only small amounts of CO_2 when it is heated with acid[1] indicates that reaction 4 is of negligible significance for CO_2 formation. It is unlikely that the platinum(IV) carbonyl (C) can be converted to $[PtH(CO)(SnCl_3)Cl]^-$ by reaction 2 with retention of CO as a ligand. Compounds of Pt(IV) with π-acceptor ligands are highly reactive,[8] and the platinum(IV) carbonyl $[Pt(CO)Cl_5]^-$ has been reported to react rapidly with water to form CO_2.[9] The observation that only small amounts of CO_2 are formed when $[Pt(CO)(SnCl_3)_2Cl]^-$ (B) is heated with HCl[1] indicates that the unstable Pt(IV) intermediate $[Pt(H)(CO)(SnCl_3)_2Cl_2]^-$ is not formed by oxidative addition of HCl (reaction 1). Oxidizing agents such as Cl_2 and Fe(III) have been used to prepare platinum(IV) carbonyl compounds.[9,10]

The change of Gibbs free energy (potential) of the Pt–Sn system is unlikely to fluctuate widely to permit significant participation of Pt in three oxidation states, Pt(0) (E and F), Pt(II) (A, B, D), and Pt(IV) (C). Compounds of Pt(0) react with SnX_4, to form platinum(II) compounds.[11] The platinum(0) compound $[Pt(PPh_3)_4]$ reacts with $SnCl_2$ and $SnCl_4$ in alcoholic solvents to form platinum(IV) hydrido complexes.[12] Platinum(0) compounds react rapidly with HCl,[10] and it is expected that Pt(0) complexes such as $Pt(SnCl_3)^-$ (E) will not have a significant lifetime in the highly acidic $HCl/HOAc/H_2O$ solvent. Intermediates E and F are thus not considered to participate significantly in the catalytic cycle.

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An "intermediate" such as F, which is a transition state for the oxidative addition of Sn(IV) to the Pt(0) compound, is typically not shown in a Tolman catalytic cycle.

A catalytic cycle for the WGS catalysis that is consistent with more recent studies[6-12] and the experimental data for the Pt–Sn system[1] is presented in Figure 2. The formation of $[Pt(CO)(SnCl_3)_2Cl]^-$ (B) from $[Pt(SnCl_3)_2Cl_2]^{2-}$ (G) in reaction 5 has been previously reported,[13] and the formation of B from $[Pt(CO)(SnCl_3)Cl_2]^-$ (A) was noted.[1] The formation of CO_2 upon heating a sample of A in the presence of $SnCl_4$ from the catalytic solution[1] is consistent with reaction 6, which is the oxidative addition of $SnCl_4$ to the platinum(II) complex B resulting in formation of the tin(II) $SnCl_3^-$ ligand and the platinum(IV) carbonyl complex $[Pt(CO)(SnCl_3)_3Cl_2]^-$ (L). The formation of CO_2 via nucleophilic attack by water on CO coordinated to platinum(IV) in reaction 7 has been discussed earlier. Reaction 8 is the intramolecular oxidation of a tin(II) $SnCl_3^-$ ligand by platinum(IV) resulting in formation of tin(IV) chloride and the platinum(II) hydrido complex $[PtH(SnCl_3)_2Cl]^{2-}$ (K). Hydridoplatinum(II) complexes with the $SnCl_3^-$ ligand have been previously reported.[14] The reduction of platinum(IV) by tin(II) in acidic solution is very rapid.[15] The protonation of the hydrido ligand (reaction 9) is a well-known reaction.[16] Chang and Eisenberg[1] reported the initial formation of larger amounts of hydrogen than CO_2 for solutions in which the Sn(II)/Pt ratio was 30/1 or 10/1. The observation is consistent with the oxidation not only by Sn(IV) but also by HCl of platinum(II) complexes such as $[Pt(SnCl_3)_2Cl_2]^{2-}$ (G) to give compounds such as J and K and subsequently hydrogen by reaction 9.

The cycle proposed for the WGS reaction shown in Figure 2 is consistent with previous studies of Pt–Sn systems and reactions involved in the homogeneous catalysis of the WGS reaction.[6a] As previously noted by Cheng and Eisenberg,[1] it is likely that the platinum intermediates have the trichlorotin ligand, but the exact nature of the intermediates in the catalytic system is unknown. The primary utility of the cycle shown in Figure 2 is to illustrate likely reaction types that can aid in explaining the experimental data and hopefully in designing better catalysts for the WGS reaction. The efficiency of the Pt–Sn system for WGS catalysis is limited by the very rapid reaction of Pt(IV) and Sn(II), which competes with the nucleophilic attack by water on the CO ligand attached to Pt(IV). Platinum compounds catalyze the oxidation of CO by Fe(III)[10] presumably because the reaction of Pt(IV) with Fe(II) is slower than the nucleophilic attack by water on a platinum(IV) carbonyl intermediate and subsequent decarboxylation.

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Registry No. K_2PtCl_4, 10025-99-7; $SnCl_4$, 7646-78-8; acetic acid, 64-19-7; hydrochloric acid, 7647-01-0.

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