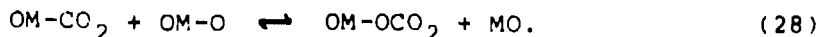
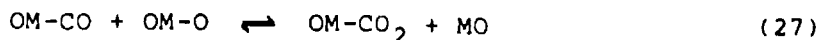


Both lattice and adsorbed oxygen may oxidize CO to CO₂ on copper oxide^{104,105} and Fe₂O₃.⁵³ On chromia, adsorbed CO and oxygen react to give carbonates and carboxyls.^{106,107} The weakly bonded CO with an infrared absorption at 2187 cm⁻¹ appears to be the reactive species.¹⁰⁶ Coadsorption of CO with oxygen on hydrated magnesia produces infrared absorptions in the carbonate region and no absorptions characteristic of adsorbed CO.^{79b} This reaction may be



The interaction between adsorbed CO and hydrogen on zinc oxide has been investigated by several groups.¹⁰⁸⁻¹¹³ The evidence is consistent with inductive strengthening of the bonds between the adsorbed species and the zinc oxide, with no new chemical bonds formed.¹¹³ These species may be more reactive than the individually adsorbed species; otherwise, this interaction is more relevant to methanation and methanol formation.

Overall Reaction Studies

Studies of the overall water gas shift reaction over iron, copper, and cobalt-molybdenum catalysts have been reviewed recently.¹¹⁴ Empirical rate equations are

summarized there and will not be considered here, although some conclusions on elementary steps in the mechanism will be reconsidered in the light of the independent evidence for the elementary reactions. The cobalt-molybdenum catalysts will not be considered here because less information exists for elementary reactions on those catalysts, and their sulfidation may introduce significant differences into the mechanism of reaction.

For the iron-chromium catalysts, two mechanisms have been proposed. The regenerative mechanism¹¹⁵ involves oxygen transfer through adsorbed oxygen atoms; this essentially consists of reactions 2 and 3 or may also include the adsorption of the other reactants. Most of the evidence for this mechanism has been obtained at higher temperatures than are of industrial interest for the water gas shift reaction, and it may be primarily of interest in metallurgy.^{118,116,117} Mechanisms proceeding through a C-H-O intermediate, such as the formate ion, have also been proposed.¹¹⁸

For the copper-zinc catalysts, most of the overall studies^{119,120} conclude that an intermediate, probably a formate,¹²⁰ is important in the mechanism. The single dissenting opinion¹²¹ is based mainly on theoretical considerations and fails to explain several points. A comparison of formate decomposition on zinc and magnesium oxides with the

water gas shift reaction led to the conclusion that formate is an important intermediate.¹⁰¹

A combined kinetic and infrared study of the water gas shift reaction on alumina¹²² showed that formate ion exists on the working catalyst and that some formate ions may not participate in the overall reaction. Infrared spectroscopy suggests that carbonate is not an important intermediate. Little if any carboxyl was observed.

Although the evidence for most of the steps is poor in terms of observed intermediates or elementary reactions, a mechanism for the water gas shift on oxide catalysts is summarized in Table IV.

HOMOGENEOUS WATER GAS SHIFT REACTION

It is not yet clear to what degree reactions observed in homogeneous metal complexes can be assumed to occur in heterogeneous systems. However, mechanisms for the water gas shift reaction have been worked out for several homogeneous systems, and some of the elementary steps appear to be similar to those in heterogeneous systems.

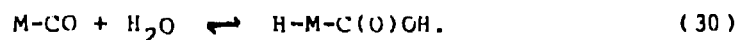
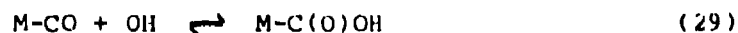
Mononuclear and polynuclear carbonyls of several transition metals catalyze the water gas shift. In acidic solution, catalysis by rhodium,¹²³ ruthenium,¹²⁴ and palladium¹²⁵ complexes has been observed, and in basic solution, by iron,¹²⁶⁻¹³⁰ nickel,¹³¹

ruthenium, 128, 129, 131-133 rhodium, 134-136 osmium, 137
iridium, 128, 137 platinum, 138, 139 and chromium,
molybdenum, and tungsten complexes. 126, 132

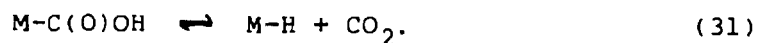
Notation can obscure the similarities between the homogeneous and heterogeneous reactions. Therefore, in this discussion reactions will be written in the notation used for the metal surfaces. Adsorbates that do not participate in the reaction will be omitted. Table V summarizes the elementary reactions suggested for the homogeneous water gas shift reaction. Reactions for both the acidic and basic media are included.

In proposing a general mechanism for the homogeneous water gas shift reaction, I will not consider charges on metal complexes. Many of the reactions take place with both neutral and charged complexes (Table V), and this simplification makes clearer the relationship to surface reactions. However, the charges will affect the energetics of the reactions and must be taken into account in calculations of specific systems.

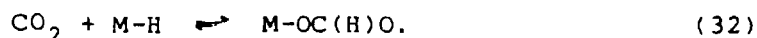
Nucleophilic attack of hydroxide or water at a carbonyl carbon has been well documented:¹⁴⁰



The metalcarboxylic acids can break down to give CO_2 :¹⁴¹



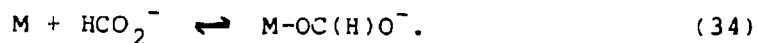
CO₂ can also react with metal complexes to give formates.¹⁴²



The equilibrium



also gives formate, which can complex with a metal:



Molybdenum hexacarbonyl reacts with formate ion to give a formatomolybdate complex and a carboxylate complex.¹⁴³

Photochemical enhancement of formate decomposition by group 6B metal hexacarbonyls¹⁴⁴ appears to support dissociation of CO from a carbonyl, followed by formate complexation and decomposition, as steps in the reaction. Both monodentate formate¹⁴⁵ and metallocarboxylic acids¹⁴¹ may be intermediates, yielding CO₂ and H₂ upon decomposition, but the metallocarboxylic acid pathway may be energetically more favorable, at least in the case of iron.¹⁴⁵

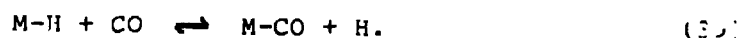
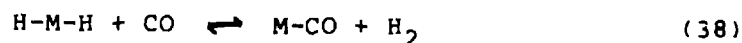
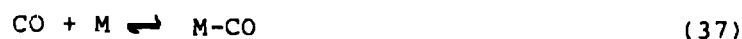
Dissociation of H₂O and formation of H₂,



are known. Addition of water to rhodium¹⁴⁶ and palladium¹⁴⁷ complexes followed by elimination of hydrogen has been observed. Another relevant reaction is the photochemical substitution of water for CO in Re₂(CO)₁₀; the

substitution proceeds through a somewhat indirect mechanism, however, with photochemical homolysis of the Re-Re bond as the first step.¹⁴⁸ Under further irradiation, the water ligand dissociates to give $\text{HRe}(\text{CO})_5$ and $\text{Re}_4(\text{CO})_{12}(\text{OH})_4$.

The addition of CO to an unsaturated metal complex or its substitution for hydrogen are both likely:



The water gas shift reaction has also been photocatalyzed with a ruthenium complex, apparently because of photo-initiation by CO dissociation from the complex.¹⁴⁹

The bicarbonate equilibrium should also be included:



CO_2 can be disproportionated to CO and carbonate by transition metal dianions,¹⁵⁰ in a reaction that may be a part of some of the homogeneously catalyzed water gas shift and suggests some aspects of the heterogeneous reaction.

A zeolite catalyst prepared from ruthenium hexamine appears to operate through a similar mechanism. Ruthenium hexamine exchanged into zeolites shows activity for the water gas shift from 90 C to 230 C.¹⁵¹ Intermediates identified by infrared spectroscopy suggest a mechanism involving

nucleophilic attack by water on CO coordinated to ruthenium to give a rutheniumcarboxylic acid.

COMPARISON OF MECHANISMS FOR DIFFERENT CONDITIONS

It should be emphasized for the following discussions that the evidence for most of the elementary reactions is incomplete. The reactions on metal surfaces, particularly CO_2 and H_2O association-dissociation, are the best supported. Many fewer studies are available for adsorption on oxides, owing to the difficulties of preparing well-characterized oxide surfaces. The adsorption-desorption reactions are fairly well established, but questions remain as to the nature of the species formed by CO and CO_2 adsorption on oxides. The steps in which the intermediate is formed and decomposed are the least supported for all mechanisms. It is not clear to what degree formate, hydroxycarboxyl, or oxygen transfer contribute to the overall reaction, although most of the evidence points to the participation of an H-C-O intermediate for the lower-temperature processes.

Considerable similarity exists among the mechanisms proposed here and previously for the water gas shift on metals, metal oxides, and in homogeneous solutions. Adsorption and desorption steps on the surfaces are similar, with the exception of physisorption, to the association reactions in

solution. In all three mechanisms, H_2 dissociates to atoms, and H_2O dissociates to hydrogen and hydroxyl. Although the reactions may be similar for CO and CO_2 adsorption, the adsorbed species on metals and oxides may have significantly different reactivities from each other and from complexed CO and CO_2 in solution. For CO on metals, backbonding weakens the C-O bond; for most oxides, backbonding is absent or almost so, and the C-O bond is strengthened relative to the gas-phase molecule. However, products of apparent nucleophilic attack on carbon are observed in all media. CO oxidation by adsorbed oxygen atoms on metals is the reverse of CO_2 dissociation. This reaction also appears likely on oxides, but less so in solution. However, it has been observed in one homogeneous system.¹⁵²

Reactions forming a C-H-O intermediate have not been observed directly on surfaces. Formic acid or a formate ion adsorbed as $M-O_2CH$ is an attractive intermediate because of the stoichiometry of formic acid and its known surface reactions:



However, the formation of adsorbed formate from CO adsorbed carbon end down requires several elementary steps of reaction with hydroxyl and rearrangement (reactions 23-25), or

reaction with oxygen and hydrogen atoms. None of these reactions have been observed. Formation from CO_2 would involve only a hydrogen transfer (reaction 26). Again, this has not been observed in heterogeneous systems. A large volume of literature, which cannot be reviewed within the scope of this paper, deals with the decomposition of formic acid on metal and metal oxide surfaces. A survey of some of the more recent of this literature shows great differences, apparently depending on the method of observation as well as the substrate. For example, most static methods show that the hydroxyl hydrogen is abstracted by metals and oxides to give surface formates,¹⁵³ but a dynamic study shows that a hydroxycarbonyl radical is formed by the abstraction of the carbon-bonded hydrogen by the metal surface and that the radical can detach from the surface.¹⁵⁴ Formation of an anhydride intermediate has been proposed,¹⁵⁵ and an anhydride has been observed by infrared reflectance spectroscopy.¹⁵⁶ However, the lack of such an observation in the $\text{H}_2\text{-H}_2\text{O-CO-CO}_2$ systems suggests that this is an unlikely pathway for the water gas shift reaction. A beta-hydride elimination has been suggested as the decomposition route from a formidorhodium complex to CO_2 and the hydrido complex.¹⁵⁷ Formic acid has also been suggested as an intermediate in the water gas shift on the basis of its overall kinetics of decomposition on a low-temperature shift

catalyst.¹²⁰ However, supporting evidence in the form of observed elementary reactions would be highly desirable.

A simpler set of elementary reactions (reactions 29-31) can be written for the CO-hydroxycarbonyl-CO₂ transformation, but few hydroxycarbonyl or carboxyl intermediates have been observed on surfaces. The observation that iron hydroxycarbonyl complexes decompose more rapidly than formido complexes¹⁴⁵ suggests that they may be the kinetically more important intermediates; their short lifetimes and consequently low steady-state concentrations may prevent their observation. On the other hand, they may be too unstable to form on surfaces.

Some of the products appear not to play a part in the water gas shift reaction except to remove a small amount of material from the system. Carbonates and the inactive form of hydrogen on oxides are in this category.

THE WATER GAS SHIFT AND THE FISCHER-TROPSCH SYNTHESIS

The water gas shift reaction is simpler than the Fischer-Tropsch synthesis. It commonly achieves equilibrium, whereas Fischer-Tropsch is at least partly controlled by kinetics. It can be represented by a conventional balanced chemical reaction, whereas Fischer-Tropsch must be represented by a generalized chemical reaction, or a collection of chemical reactions. All this points to the

probability that the water gas shift can be represented by a smaller set of elementary reactions than Fischer-Tropsch. A set of elementary reactions has been proposed for the mechanism of the Fischer-Tropsch synthesis,¹ and sets of elementary reactions have been proposed here for the mechanisms of the water gas shift reaction on metals, on oxides, and in homogeneous solution. In this section, the relationships between these two groups of elementary reactions will be examined.

Publications since the proposal of the mechanism for the Fischer-Tropsch synthesis give no reason to alter that set of elementary reactions. Adsorption of H₂ and CO on transition metals, both pure and modified with promoters and poisons, has been reviewed.¹⁵⁸ A statistical analysis to evaluate correlations between H₂ and CO dissociation and other properties of metals has also been carried out.¹⁵⁹ H₂ dissociation was found to correlate with heat of vaporization, heat of fusion, molar heat capacity, Debye temperature, atomic volume, electronegativity, first and second ionization energies, and electrical conductance. CO dissociation was found to correlate with heat of fusion, molar heat capacity, electrical conductance, and electronegativity. Several of these parameters are related to the metal-metal bond energy, and the others may relate to electronic effects.

Although attempts to observe formyl intermediates on rhodium surfaces failed,¹⁶⁰ increasing numbers of formyl metal complexes are being synthesized.¹⁶¹ The protonation route for hydrogenation has been further supported.¹⁶² Several methods of C-C bond formation have been demonstrated in complexes.¹⁶³ The reverse of C-H bond formation, the oxidative addition of hydrocarbons to iridium complexes, has been demonstrated.¹⁶⁴ Gas-phase studies of interactions between metal atoms and hydrocarbons¹⁶⁵ should give information such as bond energies that can be used in estimating rate constants for these reactions, and are showing some differences between the interactions of different metal atoms with hydrocarbons. The acidity of metal hydrides¹⁶⁶ is another set of information that will be useful in evaluating mechanisms, particularly in solution, and possibly in extrapolation to surfaces. Reactions of interest are being studied in early transition metal complexes¹⁶⁷ and actinide complexes,¹⁶⁸ but these reactions are stoichiometric rather than catalytic. Relevant organometallic reactions have been reviewed.¹⁶⁹

Several kinetic studies support the participation of carbon atoms and partially hydrogenated carbon as intermediates.¹⁷⁰ From observations of this type, it has been suggested that hydrogenolysis can be regarded as a reverse Fischer-Tropsch synthesis.¹⁷¹ Oxidation and carburization

of iron have been further studied, and it appears that some iron oxide may be present under synthesis conditions.¹⁷² Changes in kinetic regimes were observed in methanation over nickel foils¹⁷³ and in the production of hydrocarbons and oxygenates over LaRhO_3 .¹⁷⁴ Where Schulz-Flory analysis has been applied to product distributions, both consistent^{175,176} and inconsistent^{170a,173,176,177} distributions have been observed. Product distributions have been modeled for situations other than the simple Flory model, some of which are more selective.^{175,178}

Of closer relevance to the water gas shift are the nucleophilic activation of CO to reduction by hydrogen,¹⁷⁹ analogous to the nucleophilic attack by water or hydroxide proposed for the water gas shift. Coadsorption of CO and H_2 on iron¹⁸⁰ and ruthenium¹⁸¹ leads to lessened dissociation for both. Most likely, the reaction of water with surface carbon to give methane¹⁸² and the interactions among surface carbon, CO, and CO_2 ¹⁸³ are relevant to both the water gas shift and Fischer-Tropsch. However, more information is needed on the elementary reactions.

Two of the components of the water gas equilibrium, CO and H_2 , are the starting materials for the Fischer-Tropsch synthesis. The other two, CO_2 and H_2O , are products of the synthesis. However, the Fischer-Tropsch reactants are on opposite sides of the water gas equilibrium, as are the

products. Thus, the water gas shift can help or hinder the Fischer-Tropsch synthesis by altering the concentrations of reactants and products.

Since the two processes have these components in common, adsorption and desorption reactions must be shared, as must the dissociation reactions of H_2 , H_2O , and CO_2 . Aside from these reactions, there appear to be no further overlaps between the water gas shift and Fischer-Tropsch. The dissociation of CO appears not to be a part of the water gas shift. Hydroxycarbonyl may be an intermediate in acid or ester formation in Fischer-Tropsch, but evidence here is very limited. Also, if formate intermediates, which have been observed under Fischer-Tropsch conditions, are hydrogenated significantly, some of these reactions may overlap.

If the overlaps between the water gas shift and Fischer-Tropsch are limited to adsorption-desorption and association-dissociation reactions, then consideration of modifications to Fischer-Tropsch catalysts to provide oxygen rejection by H_2O rather than CO_2 may be relatively simple. Catalysts on which the H_2O association and desorption reactions are favored over the CO_2 association and desorption reactions will give a water product. Unfortunately, data for these reactions is not available for a wide range of metals.

Further applications of the relation between the water gas shift and Fischer-Tropsch are in understanding the

Kölbl-Englehardt synthesis and CO_2 methanation. The differences here are not in the elementary reactions, but in the relative concentrations of reactants and intermediates, which may give rise to different paths by effectively reducing the rate of one path to zero, while making significant another path that is inactive in the water gas shift or Fischer-Tropsch.

The overlap, however, of the association-dissociation and adsorption-desorption reactions between the water gas shift and Fischer-Tropsch means that it is not useful to separate these two processes conceptually. The water gas shift, although a simpler set of elementary reactions than Fischer-Tropsch, cannot itself be regarded as an elementary reaction. An attempt at a mathematical separation of the kinetics of the water gas shift from the kinetics of Fischer-Tropsch will give meaningless results because the sets of elementary reactions are not orthogonal. Thus, the shorthand of attributing various effects observed in the Fischer-Tropsch synthesis to the water gas shift should be avoided, and an attempt should be made to attribute the effects to a particular elementary reaction or set of elementary reactions.

METHANOL SYNTHESIS

Although the scope of this paper does not permit a detailed discussion of methanol synthesis, that reaction must be closely related to the water gas shift over the low-temperature catalyst, since the catalysts are similar. An ideal situation would be to be able to write a list of elementary reactions encompassing both methanol synthesis and the water gas shift. However, the intermediates in methanol synthesis have not been unambiguously identified.¹⁸⁴ Clearly the largest difference between the two processes is in the oxidizing power of the reactants: synthesis gas for methanol is more reducing than either side of the water gas equilibrium. However, small amounts of CO_2 promote methanol synthesis. Again, as in the Fischer-Tropsch synthesis, adsorption-desorption of H_2 , H_2O , CO , and CO_2 and association-dissociation reactions of H_2 , H_2O , and CO_2 are probably common to both processes. The CO that is hydrogenated to methanol remains associated, as is likely for the CO that is oxidized in the water gas shift. As is the case in the water gas shift, it is not clear whether the intermediates in CO hydrogenation are bonded to the catalyst through oxygen (formate-methoxy route) or through carbon (formyl-hydroxymethyl route), or whether both of these routes are significant.¹⁸⁵

SUMMARY AND OUTLOOK

The water gas shift shares a significant number of elementary reactions with the Fischer-Tropsch synthesis, and probably with the Kölbel-Engelhardt synthesis, CO₂ methanation, and methanol synthesis. Oxygen transfer from CO₂ or H₂O to the catalyst and then to H₂ or CC may be the predominant route at higher temperatures in heterogeneous systems and appears to be possible for homogeneous systems. However, a C-H-O intermediate also participates at lower temperatures, particularly in homogeneous systems. This intermediate may be formate or hydroxycarbonyl, but little information now exists that can clarify whether one or both are important.

More information is needed about the interactions of H₂, H₂O, CO, and CO₂ on well-characterized oxide surfaces. Studies of formic acid as a model compound may also be useful, but caution is necessary in their interpretation. The relationship of homogeneous reactions to heterogeneous catalysis is still not clear, but the parallels in the water gas shift appear to be significant. Again, more studies of the intermediates on surfaces will help to elucidate this relationship.

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