

Homogeneous transition metal catalysis: from the water gas shift reaction to nuclear waste vitrification

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Dedicated to: Professor László Markó on the occasion of his 70th birthday in recognition of his outstanding contributions to organometallic chemistry and molecular catalysis.

Abstract

A US–Hungarian cooperative research project between Professor R. Bruce King at the University of Georgia and Professor László Markó at the University of Veszprém during the period 1977 to 1986 was a major stimulus in extending the scope of Professor King's research at the University of Georgia from synthetic transition metal organometallic chemistry to homogeneous catalysis. Since that US–Hungarian cooperative research project, a major emphasis of the work on homogeneous catalysis at the University of Georgia has been on applications of homogeneous transition metal catalysis to carbon monoxide, formate, and formic acid chemistry. This started with a joint project of Professor R. Bruce King with Professor Allen D. King Jr., which led to the discovery of an interesting mechanistic duality for the metal carbonyl-catalyzed water gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) where use of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) catalyst precursors leads to a dissociative mechanism through formate metal carbonyl intermediates whereas use of an $\text{Fe}(\text{CO})_5$ catalyst precursor leads to an associative mechanism through metalcarboxylate intermediates. Subsequent scientific interaction of Professor R. Bruce King with Dr Charles M. King, then of the Westinghouse Savannah River Technical Center, led to a study of related formic acid reactions occurring during pre-treatment of nuclear wastes arising from catalytic activities of noble metal species in the wastes generated from uranium fission. Thus research at the University of Georgia during the period 1991–1994, supported through funding from the Savannah River and Hanford nuclear sites, led to the identification of a homogeneous nitrorhodium-catalyzed process for hydrogen liberation from formic acid with an apparent mechanism similar to the dissociative mechanism for the water gas shift reaction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Tungsten; Chromium; Molybdenum; Rhodium; Homogenous catalysis; Water gas shift reaction; Hydrogenation; Nuclear waste treatment

1. Introduction

The initial research of my scientific career dating back from my graduate school days at Harvard University with Professor F.G.A. Stone during 1957–1961 involved fundamental studies on the synthesis of novel transition metal organometallic compounds [1]. I continued active work in this area at E.I. du Pont

de Nemours and Co. during 1961–1962, at the Mellon Institute (now part of Carnegie–Mellon University) during 1962–1966, and at The University of Georgia following my move there in 1966. However, in the 1970s there became increasing pressure to develop practical applications for this area of fundamental research. A natural application was the area of homogeneous catalysis, i.e. the use of soluble transition metal complexes to catalyze reactions of practical importance. Interest in homogeneous catalysis in the 1970s was also stimulated by the oil crises of 1973 and 1977, which created the need to develop energy sources not dependent on fossil fuels as well

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as energy efficient methods of chemical synthesis. This led to increased research funding opportunities from the US government through what was initially the Energy Research and Development Administration (ERDA) and subsequently the Department of Energy (DOE).

My initial research on homogeneous catalysis and related topics at The University of Georgia was funded by two joint contracts from ERDA with other The University of Georgia faculty members. The first such project, in collaboration with Professors Charles Kutal and Richard Hautala, involved the development of a solar energy storage system based on the norbornadiene–quadricyclane valence isomerization [2]. The other project in collaboration with Professor Allen D. King Jr. (no relation) initially involved an infrared spectroscopic study of transition metal carbonyl chemistry under high carbon monoxide pressure but soon turned to a mechanistic study of the water gas shift and related reactions [3]. The latter project led to a long-standing interest in the transition metal catalysis of carbon monoxide and formate reactions that has continued well into the 1990s. Initially the practical impetus for this work was the use of synthesis gas (1:1 CO/H₂) from coal and steam as a substitute for fossil fuels as an energy source and chemical feedstock. In the 1990s the impetus for this work moved to a major environmental problem, namely the development of methods of immobilizing the large amount of high activity nuclear wastes accumulated in the US at the Savannah River Site near Aiken, South Carolina, and the Hanford Site near Richland, Washington, into glass logs in order to minimize their long-term environmental impact. The use of formic acid as a reasonably strong reducing acid had been planned for the pretreatment of such nuclear wastes prior to their vitrification. However, undesirable side reactions of formic acid created difficulties in designing a viable and safe process. During the period 1991–1994, I had research contracts, first with the Savannah River Site and then with the Hanford Site (through the Pacific Northwest National Laboratory), to study at The University of Georgia the reactions of formic acid catalyzed by the noble metal fission products Ru, Rh, and Pd in non-radioactive simulated nuclear waste media.

This article summarizes the highlights of the work on homogeneous transition metal-catalyzed reactions of carbon monoxide, formate, and formic acid starting with the work on the water gas shift and related reactions in the 1970s and continuing with work in the 1990s on noble metal-catalyzed reactions of formic acid in simulated nuclear waste media. Further details are given in the cited references.

2. The “Hungarian connection” with Professor Markó’s laboratory

Early in my career, it was already apparent that highly significant research at the interface of transition metal organometallic chemistry and homogeneous catalysis was being done in the laboratory of Professor László Markó in Veszprém, Hungary, at the Research Group for Petrochemistry of the Hungarian Academy of Sciences and the Veszprém University of Chemical Engineering (now the University of Veszprém). Collaboration with Professor Markó’s laboratory appeared to be a possible entry into some exciting areas of homogeneous transition metal catalysis. However, in the early stages of my scientific career I had some reservations, for political reasons, for becoming involved in research in a then-Communist country and concentrated my research efforts elsewhere. Even in the 1960s, I was especially concerned about the situation in Hungary since when I took a 14-week ‘grand tour’ of Europe as a graduate student in 1958, the US passport that I had was stamped in black bold letters “not valid for travel in Hungary” and my only foray then into the then-Communist world was into the Yugoslavia of Tito, with the easternmost points of the grand European tour being Belgrade, Sarajevo, and Dubrovnik. Also the only demonstration in which I ever participated in my life was in 1956 in Cleveland, Ohio, as an 18-year old undergraduate at Oberlin College in Ohio, where I was part of a group of Oberlin students protesting the events of the 1956 Hungarian revolution.

My first scientific connection with the group in Veszprém, Hungary, was not with Professor Markó but with Professor Gyula Pályi (now at the University of Modena in Italy), who approached me in 1974 about some joint work on the carbonyl stretching frequencies of C₃H₅V(CO)₄ and CH₃COV(CO)₄, which were compounds available in my laboratory at that time. I gladly provided him with samples of these two vanadium compounds and his work on them led to an eventual joint publication [4]. When the details of this publication were finalized at the International Conference on Organometallic Chemistry in Venice, Italy, in August, 1975, I also had discussions with Professor László Markó and other members of his group which ultimately led to a US–Hungarian cooperative research project on molecular catalysis, which was funded by the US National Science Foundation and corresponding Hungarian agencies (ultimately the Hungarian Academy of Science) for the period 1977–1985. The first phase of this cooperative project involved one-year visits of two Hungarians (Drs József Bakos and Sándor Vastag) to The University of Georgia and two Americans (Drs Carl Hoff and Nicholas Takach) to the University of Veszprém. The

second and final phase of this project was expanded to include other faculty members at both The University of Georgia (Professors John Garst and Allen King) and the University of Veszprém (Professors Ferenc Ungváry and Bálint Heil). Even though this cooperative project formally ended in 1985, some of the scientific collaborations established during that project have continued until the present time. Most notably, Professor Ungváry continues to spend most summers at The University of Georgia working with Professor Garst. Also the two Americans spending a year in Hungary during the initial phase of this project, namely Professors Hoff and Takach, now at the Universities of Miami and Tulsa, respectively, obtained the 'ultimate souvenir' from their visits to Hungary, namely Hungarian wives.

The research carried out during the first part of the US–Hungarian cooperative research project on molecular catalysis was in an area outside the scope of this article, namely the development of chiral phosphines for asymmetric catalysis. The general idea of this initial research was the extension of methods developed at The University of Georgia in the late 1960s and early 1970s for the synthesis of polytertiary phosphines [5] to chiral ligands and to use rhodium(I) complexes of such ligands for the asymmetric hydrogenation of various type of prochiral substrates [6]. When the scope of the cooperative research project was broadened in 1981, topics relating to the catalysis of carbon monoxide reactions, particularly the hydroformylation reaction, were also studied. This led to key results on the kinetics of reactions of alkylcobalt carbonyls similar to intermediates in hydroformylation reactions [7] as well as CIDNP evidence for radical intermediates in the hydroformylation and reduction of styrene by $\text{HCo}(\text{CO})_4/\text{CO}$ [8].

3. The metal carbonyl-catalyzed water gas shift reaction

An important raw material for modern technology is synthesis gas, the 1:1 CO/H_2 mixture obtained from coal and steam (Fig. 1). Further reactions of synthesis gas can provide methods for the manufacture of hydrocarbons such as methane and gasoline as well as alcohols and glycols. In addition, enrichment in H_2 at the expense of CO of the CO/H_2 mixture obtained from coal and steam by the water gas shift reaction (Eq. (1)) can provide a source of H_2 for other manufacturing processes such as the manufacture of ammonia by the Haber process (Fig. 1).



Traditional synthesis gas chemistry has frequently used heterogeneous catalysts. For example, the water gas shift reaction (Eq. (1)) can be carried out at temper-

atures $> 300^\circ\text{C}$ using heterogeneous catalysts consisting of iron oxides promoted by Cr_2O_3 . Other heterogeneous catalysts for the water gas shift reaction include Fe_3O_4 above 350°C or copper metal at $200\text{--}250^\circ\text{C}$ [9].

The 'modern' era of homogeneous catalysis of the water gas shift reaction dates from the 1977 publication of Laine, Rinker, and Ford [10], who discovered that a catalyst generated from $\text{Ru}_3(\text{CO})_{12}$ and KOH catalyzed the water gas shift reaction (Eq. (1)) at fairly low temperatures, e.g. around 100°C . Subsequently, the late Pettit et al. [11] found that triethylamine could be substituted for KOH as the base and that $\text{Rh}_6(\text{CO})_{16}$ could be substituted for $\text{Ru}_3(\text{CO})_{12}$. This latter result was already reported a decade earlier in the Soviet literature by Imyanitov et al. in 1967 [12], but workers in the USA and other Western countries studying the homogeneously catalyzed water gas shift reaction in the late 1970s apparently were completely unaware of this earlier report. For example, I personally became aware of Imyanitov's 1967 paper only through a personal communication from Professor Imyanitov after I presented an earlier version of our work reported in the current paper at a workshop held on the Gleb Krzhizhanovski Volga River ship in Russia in May, 1994 [13].

The initial work in 1977 [9,10] was soon followed by subsequent work showing that non-cluster noble metal compounds can also be used as homogeneous catalysts for the water gas shift reaction and that such reactions do not require basic media. Thus during the period 1977–1978 Eisenberg et al. discovered homogeneous water gas shift catalysts based on both the $[\text{Rh}(\text{CO})_2\text{Cl}]_2/\text{CH}_3\text{CO}_2\text{H}/\text{HCl}/\text{NaI}$ system [14] and the

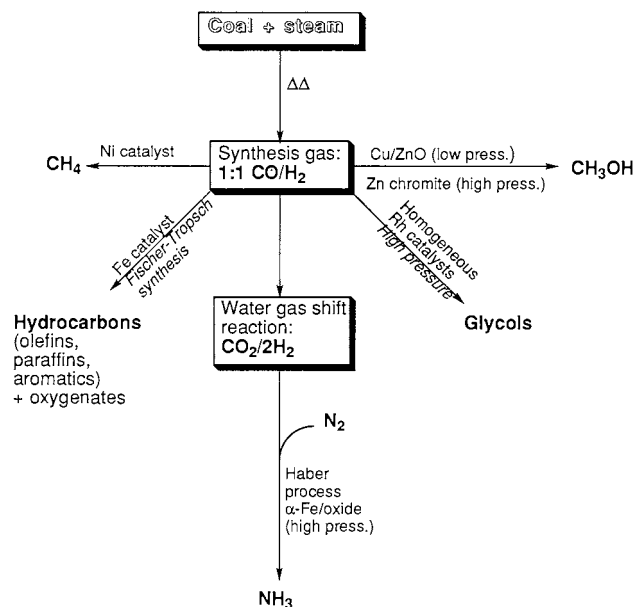


Fig. 1. Synthesis gas (1:1 CO/H_2) from coal and steam as a raw material.

$K_2PtCl_4/SnCl_4/CH_3CO_2H/HCl$ system [15]. These catalyst systems were active at 90°C and $p_{CO} = 400$ Torr. In 1978, Otsuka et al. [16] reported that $(iPr_3P)_3Pt$ was an active catalyst for the water gas shift reaction in acetone solution at 150°C and $p_{CO} = 20$ atm.

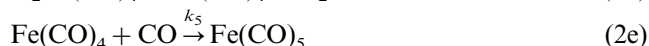
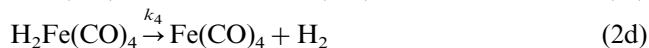
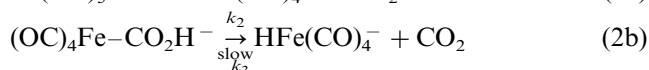
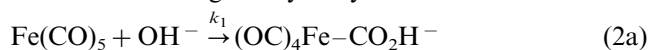
In late 1977, we initiated our work on the metal carbonyl-catalyzed water gas shift reaction at The University of Georgia. Our studies were carried out in type 304 stainless steel autoclaves with an internal volume of 700 ml, equipped with a Fisher Flexo-Mix magnetic stirrer with a 1 inch (2.5 cm.) Teflon coated magnetic bar. The gas phase was analyzed using a Fisher model 1200 gas partitioner with a 2 m, 80–100 mesh column filled with Columnpak PQ in series with a 3.3 m 13X molecular sieve column attached to a Varian CDS 111 digital integrator using helium as the carrier gas and argon as an internal standard. In this system at 140°C using 200 ml liquid loadings an increment of 1 psi (0.0068 MPa) coincidentally corresponded to approximately 1 mmol of gas.

Using this apparatus we demonstrated the catalytic activity of systems derived from simple mononuclear carbonyls for the water gas shift reaction (Eq. (1)) as illustrated by the following two experiments [17]:

(1) A solution of 0.3 ml (0.45 g., 2.23 mmol) of $Fe(CO)_5$, 2.6 g. (65 mmol) of NaOH, 190 ml of *n*-butanol, and 10 ml of water at 170–180°C and $p_{CO} = 28.2$ atm led to a H_2 production rate (measured as turnover number) of 140 mole of H_2 /mol of $Fe(CO)_5$ per day.

(2) A solution of 0.0442 g (0.126 mmol) of $W(CO)_6$, 20 ml of 10 *M* aqueous KOH, and 100 ml of methanol at 170°C and $p_{CO} = 7.7$ atm led to a turnover number of 920 mol of H_2 /mol of $W(CO)_6$ per day. This reaction was carried out to the point at which 66% of the CO originally introduced had reacted.

Hydrogen production from the iron carbonyl-catalyzed water gas shift reaction was found to be first-order in $[Fe(CO)_5]$, zero-order in $[CO]$, and essentially independent of base concentration because of the formate buffer system [18]. This suggests a mechanism with the following catalytic cycle:



This mechanism is called an *associative mechanism*, since the metal carbonyl precursor $Fe(CO)_5$ enters the catalytic cycle through a second-order reaction with OH^- to give the metalcarboxylate intermediate $(OC)_4Fe-CO_2H^-$ (see Eq. (2a)). Application of the steady-state approximation to this mechanism (Eqs. (2a–e)) leads to the following rate equation:

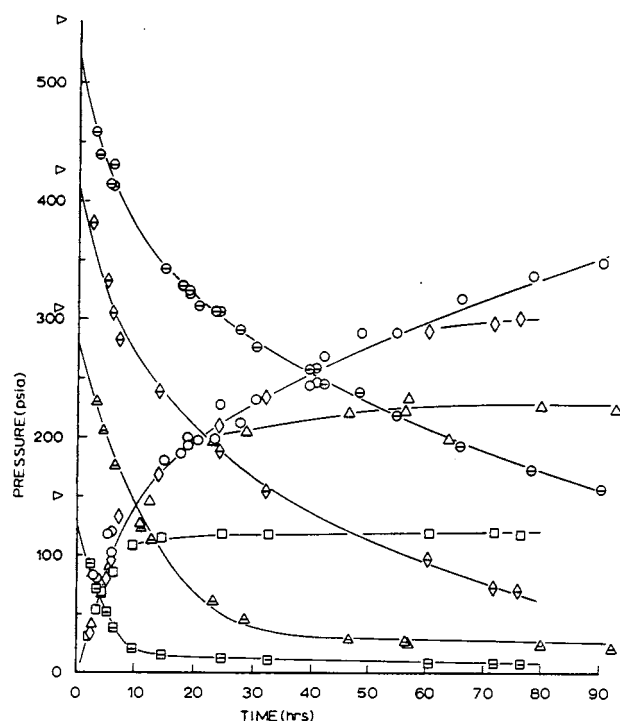


Fig. 2. Partial pressures of H_2 and CO as a function of time for a series of iron carbonyl experiments differing only with respect to the loading pressure of CO. Catalyst solution: $Fe(CO)_5$ (2.23 mmol), KOH (39 mmol), 200 ml 25% $H_2O/75\%$ CH_3OH ; temperature 140°C; loading pressures of CO corrected to 140°C: ○, 556; ◇, 425; △, 309; □, 150 psi.

$$\frac{d[H_2]}{dt} = k_1[Fe(CO)_5][OH^-] \quad (3)$$

Eq. (3) accounts for the observed first-order dependence in $[Fe(CO)_5]$ as well as the zero-order dependence in $[CO]$.

The iron carbonyl catalyst system requires a certain minimum CO pressure in order to maintain its catalytic activity (Fig. 2) and appears to decompose when the CO pressure falls below this critical minimum. Thus the water gas shift reaction was found to stop when the partial pressure of CO fell below 50 to 100 psi (approx 3–7 atm) apparently owing to catalyst decomposition. The stoichiometry of this catalyst decomposition was investigated by measuring, at low CO pressures, the production of H_2 in excess of that produced from CO by the water gas shift reaction (Fig. 3), i.e. the mmol of H_2 in excess of the mmol of CO converted to CO_2 . Thus experiments at 110°C with 2.23 mmol and 4.46 mmol of $Fe(CO)_5$ at 110°C at loading pressures of CO of 13.2 ± 0.6 psi using 58 mmol of sodium formate as the base in 200 ml of 75% $CH_3OH/25\%$ H_2O gave 12 mmol and 23 mmol, respectively, of H_2 corresponding to $H_2/Fe(CO)_5$ ratios of 5.4 and 5.2, respectively. This corresponds approximately to the decomposition of $Fe(CO)_5$ under these conditions according to the following general equation, which predicts the generation of 6 mol H_2 /mol $Fe(CO)_5$:

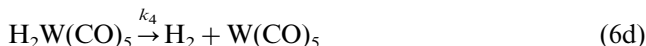
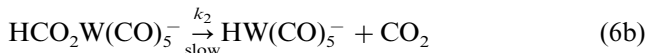
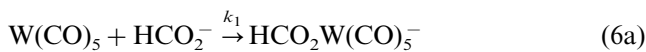


Eq. (4) suggests that one molecule of $\text{Fe}(\text{CO})_5$ can be regarded as a source of 12 electrons in a redox system with two of the electrons coming from the $\text{Fe}^0 \rightarrow \text{Fe}^{\text{II}}$ oxidation and the other ten electrons coming from oxidizing each of the five CO groups of $\text{Fe}(\text{CO})_5$ to CO_2 .

The kinetics of the tungsten carbonyl-catalyzed water gas shift reaction [19] were found to be significantly different from those of the iron-carbonyl-catalyzed water gas shift reaction discussed above. Thus hydrogen production from the tungsten carbonyl-catalyzed water gas shift reaction was found to be first-order in $[\text{W}(\text{CO})_6]$, inverse first-order in $[\text{CO}]$ (Fig. 4), and first-order in base concentration. This corresponds to a first-order reaction in $[\text{HCO}_2^-]$ since formate can be generated rapidly from a base and CO according to the following equation:



The experimental data suggest the following catalytic cycle involving tungsten carbonyl species and formate generated by Eq. (5) above:



The coordinately unsaturated $\text{W}(\text{CO})_5$ fragment required for the above catalytic cycle (Eqs. (6a–d)) can

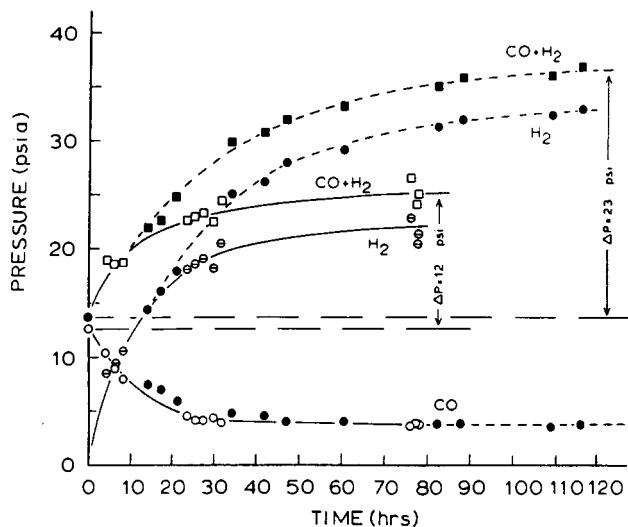


Fig. 3. Partial pressures of H_2 and CO as a function of time for iron carbonyl reactions carried out at low pressures of carbon monoxide. Catalyst solution: HCO_2Na (58 mmol), 200 ml 25% $\text{H}_2\text{O}/75\%$ CH_3OH ; temperature 110°C . Open symbols: $\text{Fe}(\text{CO})_5$, 2.23 mmol; solid symbols: $\text{Fe}(\text{CO})_5$, 4.46 mmol. Loading pressures of CO corrected to 110°C : open symbols 12.6 psi; solid symbols, 13.7 psi.

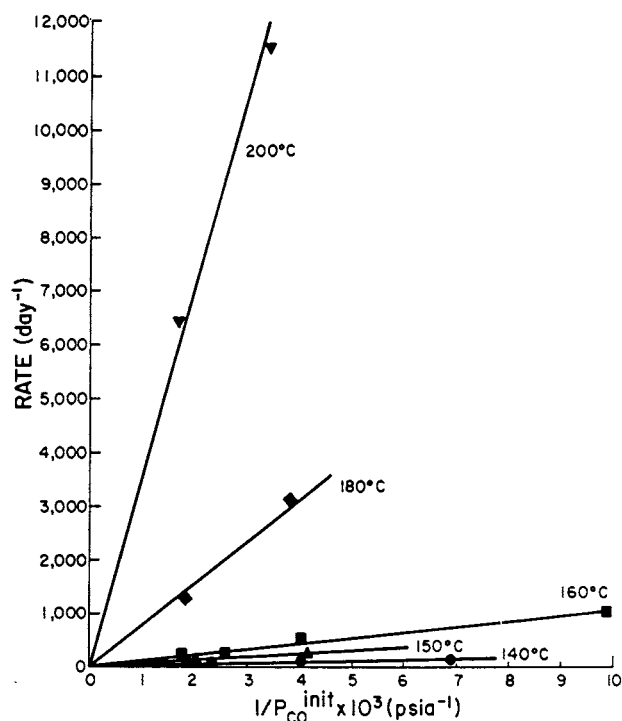
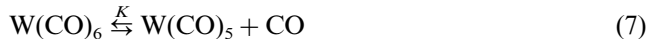


Fig. 4. Rate of H_2 production from a catalyst system containing $\text{W}(\text{CO})_6$ measured at constant base concentration as a function of $1/P_{\text{CO}}^{\text{init}}$. Catalyst solution: $\text{W}(\text{CO})_6$ (0.126 mmol), KOH (39 mmol), 200 ml 25% $\text{H}_2\text{O}/75\%$ CH_3OH .

be generated by dissociation of the $\text{W}(\text{CO})_6$ catalyst precursor:



Furthermore the intermediate $\text{H}_2\text{W}(\text{CO})_5$ is most likely a six-coordinate dihydrogen complex (H_2) $\text{W}(\text{CO})_5$ rather than a seven-coordinate dihydride (H_2) $\text{W}(\text{CO})_5$. Dihydrogen complexes [20] of the general type $(\text{R}_3\text{P})_2\text{W}(\text{CO})_3(\text{H}_2)$ derived from the proposed (H_2) $\text{W}(\text{CO})_5$ by replacement of two of the five CO groups with bulky phosphine ligands (e.g. $\text{R} = i\text{Pr}$) were first reported by Kubas in 1984 [21] three years after our 1981 publication on the kinetics of the tungsten carbonyl-catalyzed water gas shift reaction.

The mechanism for the tungsten carbonyl-catalyzed water gas shift reaction summarized above (Eqs. (5–7)) is called a *dissociative mechanism*, since the metal carbonyl precursor $\text{W}(\text{CO})_6$ enters the catalytic cycle through dissociation of one carbonyl group to give the co-ordinately unsaturated intermediate $\text{W}(\text{CO})_5$ (Eq. (7)). Application of the steady-state approximation to this mechanism leads to the following rate equation:

$$\frac{d[\text{H}_2]}{dt} = K k_1 \frac{[\text{M}(\text{CO})_6][\text{HCO}_2^-]}{[\text{CO}]} \quad (8)$$

This rate equation accounts for the observed first-order dependence on $[\text{W}(\text{CO})_6]$, inverse first-order dependence on $[\text{CO}]$ (Fig. 4), and first-order dependence on the base concentration.

Sulfur-containing impurities are expected to be present in many synthesis gas feedstocks for a water gas shift reactor. For this reason the sulfur tolerance of the water gas shift catalysts were measured using Na_2S as the sulfur source, which generates H_2S by the following hydrolysis reactions [22]:



The following observations were made (Table 1):

(1) With KOH as the base, the 4d transition metal carbonyls (Mo, Ru) exhibit maximum catalytic activity compared with the corresponding 3d and 5d transition metal carbonyls.

(2) Among the carbonyl derivatives of each periodic group (Cr, Mo, W) and (Fe, Ru, Os) inhibition of catalytic activity by sulfur diminishes with increasing atomic number of the central metal atom.

4. Iron carbonyl-catalyzed olefin reactions

A natural extension of the iron carbonyl-catalyzed water gas shift reaction is the Reppe hydroformylation of ethylene to produce propionaldehyde and 1-propanol according to the following reactions [23]:

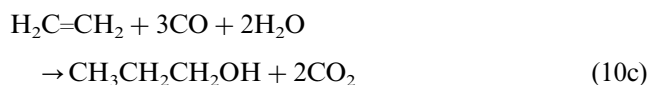
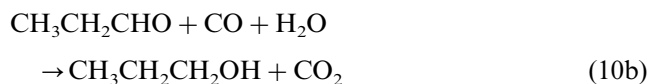
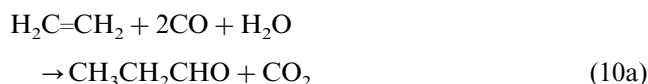


Table 1
Sulfur tolerance of the water gas shift reaction catalysts^a

Metal carbonyl ^b	Rate with KOH ^c	Rate with Na_2S ^c	$\frac{\text{Na}_2\text{ rate}}{\text{KOH rate}}$ (%)
$\text{Cr}(\text{CO})_6$ (0.13)	490	60	12
$\text{Mo}(\text{CO})_6$ (0.13)	790	130	16
$\text{W}(\text{CO})_6$ (0.13)	280	180	64
$\text{Fe}(\text{CO})_5$ (2.23)	650	0	0
$\text{Ru}_3(\text{CO})_{12}$ (0.021)	870	550	63
$\text{Os}_3(\text{CO})_{12}$ (0.021)	210	200	95

^a Each experiment was identical with respect to CO loading pressure (400 psi \approx 13.3 atm at 25°C) and solvent (200 ml $\text{H}_2\text{O}/\text{MeOH}$, 25:75 v/v) containing 39 mmol of KOH or 58 mmol of Na_2S , respectively. The experiment with $\text{Fe}(\text{CO})_5$ was conducted at 140°C and all others at 160°C.

^b mmol used given in parentheses ().

^c $\frac{\text{mol H}_2 \text{ per day}}{\text{mol metal carbonyl}}$

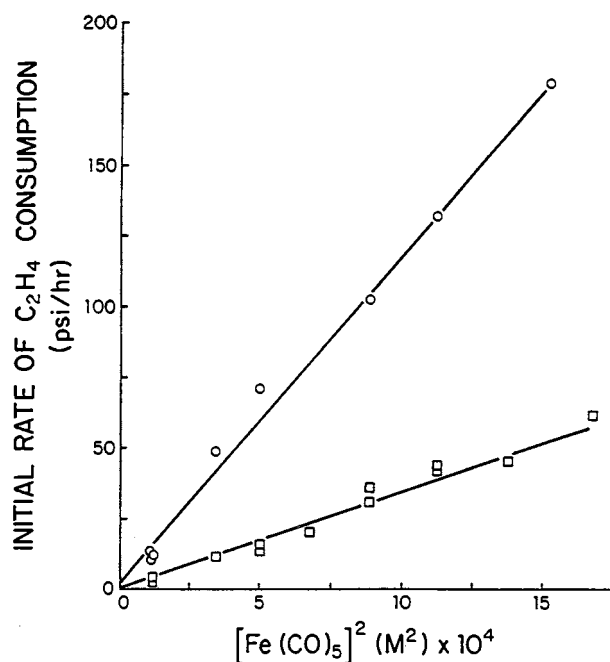
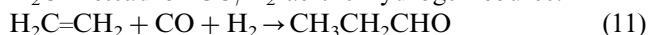


Fig. 5. Initial rate of ethylene consumption as a function of $[\text{Fe}(\text{CO})_5]^2$. Catalyst solution: $\text{Fe}(\text{CO})_5$ (variable), KOH (36 mmol), 200 ml 25% $\text{H}_2\text{O}/75\%$ CH_3OH ; temperatures 110 and 120°C; initial partial pressure of CO: 361 ± 8 psi; initial partial pressure of C_2H_4 : 120 ± 4 psi. ○ \Rightarrow $T = 120^\circ\text{C}$; □ \Rightarrow $T = 110^\circ\text{C}$.

The first step (Eq. (10a)) is closely related to the hydroformylation of ethylene (Eq. (11)) but using $2\text{CO}/\text{H}_2\text{O}$ instead of CO/H_2 as the hydrogen source.



The second step (Eq. (10b)) involves the hydrogenation of an aldehyde to the corresponding alcohol but again uses $\text{CO}/\text{H}_2\text{O}$ as a water gas shift derived hydrogen source. Reaction (10c) is the sum of reactions (10a) and (10b). Since these reactions use the water gas shift reaction (Eq. (1)) as the hydrogen source, they can be carried out under essentially the same conditions as the iron carbonyl-catalyzed water gas shift reaction discussed above but with addition of ethylene to the gas mixture.

The kinetics of the Reppe hydroformylation reaction [24] were studied in the 110–140°C temperature range using the same methodology as our earlier studies of the water gas shift reaction. Propionaldehyde formed by Eq. (10a) was found to be the principal product when NaOH was used as the base. An unusual feature of the kinetics of this reaction was the second-order dependence of its rate on the $[\text{Fe}(\text{CO})_5]$ concentration (Fig. 5) suggesting involvement of a binuclear iron carbonyl intermediate. The rate of the reaction was found to increase with ethylene concentration and to be inhibited by $[\text{CO}]$. Infrared spectra indicate that $\text{HFe}(\text{CO})_4^-$ and $\text{Fe}(\text{CO})_5$ are present in the solution phase under the reaction conditions.

The experimental observations on the kinetics of the Reppe hydroformylation noted above [24] are consistent with the mechanism depicted in Fig. 6. The rate determining step of this mechanism involves the combination of two mononuclear iron carbonyl derivatives to form a binuclear iron carbonyl derivative in accord with the observed second-order dependence of the reaction rate on the $[\text{Fe}(\text{CO})_5]$ concentration. In Fig. 6 this rate-determining step is the oxidative addition of $\text{HFe}(\text{CO})_4^-$ to $\text{CH}_3\text{CH}_2\text{COFe}(\text{CO})_3^-$ to give the binuclear complex $(\text{CH}_3\text{CH}_2\text{CO})\text{Fe}(\text{CO})_3(\text{H})\text{Fe}(\text{CO})_4^-$, which can readily eliminate propionaldehyde to give $\text{Fe}_2(\text{CO})_7^-$. The related cobalt carbonyl reaction $\text{EtOOCCH}_2\text{Co}(\text{CO})_4 + \text{HCo}(\text{CO})_4$ was studied as part of the US–Hungarian cooperative research project [7] and found to give ethyl acetate and $\text{Co}_2(\text{CO})_8$, presumably through reductive elimination of the ethyl acetate from a similar binuclear adduct of the type $(\text{EtOOCCH}_2)\text{Co}(\text{CO})_4(\text{H})\text{Co}(\text{CO})_3$. This cobalt carbonyl chemistry is closely related to the iron carbonyl chemistry of the Reppe hydroformylation reaction (Fig. 6) through the isoelectronic substitution $\text{Fe}^- \leftrightarrow \text{Co}$.

The product distribution from the Reppe hydroformylation was found to depend upon the base used in conjunction with the iron carbonyl catalyst system. Thus the substitution of Et_3N for NaOH facilitates the reduction of propionaldehyde to form 1-propanol but results in a slower rate for the overall reaction. Fig. 7 shows a possible mechanism for the hydrogenation of aldehydes to alcohols using the $\text{HFe}(\text{CO})_4^-/\text{Et}_3\text{N}$ system. The fact that the ability of Et_3N to facilitate reduction of propionaldehyde to 1-propanol is greater

than that of NaOH relates to the ability of the conjugate acid, Et_3NH^+ , to function as a proton source.

Some studies were done during the course of the US–Hungarian cooperative research project on the hydrogenation of ethylene to ethane catalyzed by $\text{Fe}(\text{CO})_5$ in Et_3N solution [25]. In this case a non-aqueous system was used so that H_2 rather than the water gas shift derived $\text{CO}/\text{H}_2\text{O}$ was the hydrogen source. Thus in a typical experiment, the 700 ml stainless steel autoclave was charged with a catalyst solution consisting of 3.0 ml (25 mmol) of $\text{Fe}(\text{CO})_5$ and 100 ml (710 mmol) of Et_3N . The system was then pressurized with a gas mixture consisting of 100 psi of $\text{H}_2\text{C}=\text{CH}_2$, 600 psi of H_2 , and 50 psi of CO and heated to 170°C . The CO was used in the system in order to prevent decomposition of the catalyst system. The progress of the reaction, as usual, was monitored by gas chromatography. Formation of ethane under these conditions was observed at a rate of 10 psi h^{-1} corresponding to an ethane turnover number of $0.44/\text{Fe}(\text{CO})_5/\text{h}$.

The sensitivity of this reaction was studied as a function of the concentration (pressure) of the reactants H_2 and $\text{H}_2\text{C}=\text{CH}_2$ as well as the CO used to stabilize the catalyst system. Since a manifold system that would allow careful control over each partial pressure was not available, it was not possible to conduct a series of experiments holding one or more partial pressures constant as is done traditionally in kinetic experiments such as these. Therefore we were forced to use randomly varied gas compositions and linear regression methods to determine the order of the reaction with respect to the various gas species.

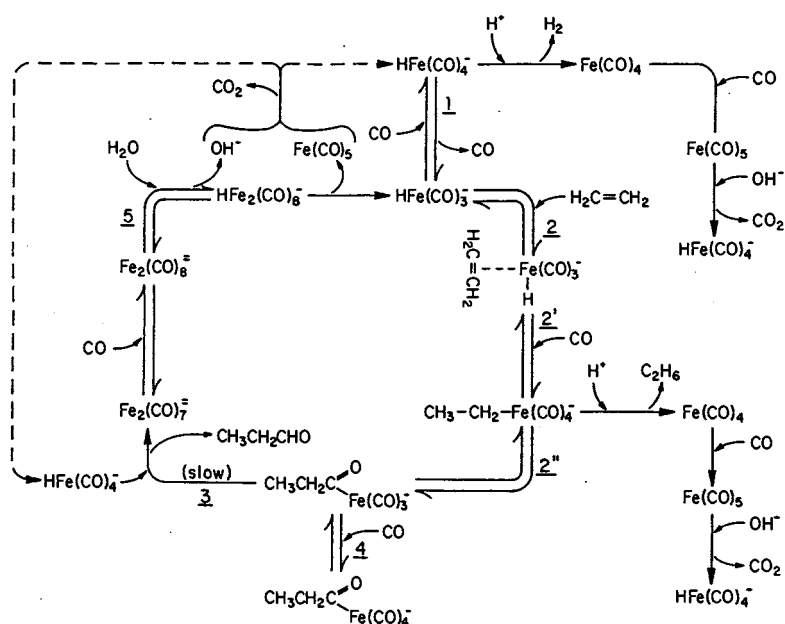


Fig. 6. A proposed mechanism for the iron carbonyl-catalyzed Reppe hydroformylation.

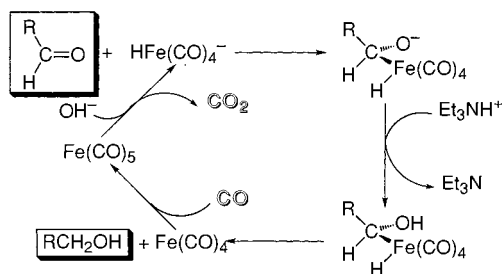


Fig. 7. A possible mechanism for the hydrogenation of aldehydes to alcohols using the $\text{HFe}(\text{CO})_4^-/\text{Et}_3\text{N}$ system.

Within the large error limits inherent in this method, the reaction appeared to be first-order in $\text{H}_2\text{C}=\text{CH}_2$ and zero-order in H_2 . The CO appeared to inhibit the reaction in a well-defined inverse first-order manner consistent with a mechanism involving loss of CO to generate coordinately unsaturated intermediates. The activation energy of this reaction estimated from changes in reaction rate in the temperature range 130–170°C was estimated to be 23 kcal mol⁻¹. A search for catalytic intermediates using infrared spectroscopy under the reaction conditions in a high-pressure infrared cell failed to detect significant concentrations of any iron carbonyl hydride derivatives such as $\text{H}_2\text{Fe}(\text{CO})_4$ and $\text{HFe}(\text{CO})_4^-$.

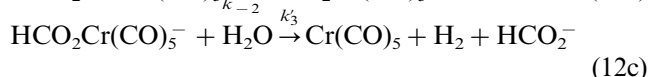
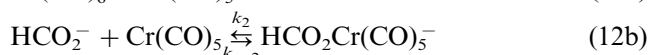
5. Formate reactions photocatalyzed by chromium carbonyl

The involvement of the formate ion generated from $\text{OH}^- + \text{CO}$ by Eq. (5) in the water gas shift reaction catalyzed by the group 6 metal carbonyls (Eqs. (6a–d)) suggested that the metal hexacarbonyls $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) might be effective catalyst precursors for formate reactions in the presence of light to facilitate their dissociation to reactive $\text{M}(\text{CO})_5$ fragments (see Eq. (7)). In this connection in 1981 [26] we first observed the photolytic generation of H_2 from formate in the presence of $\text{W}(\text{CO})_6$ in aqueous methanol. The rate of H_2 production (Fig. 8) was found to exhibit saturation kinetics in formate ion and to be inhibited by added pyridine [27].

Evidence for the involvement of $\text{LCr}(\text{CO})_5$ intermediates in this reaction were also provided by a study of the infrared $\nu(\text{CO})$ frequencies of the reaction solution upon ultraviolet irradiation in a closed system (Fig. 9). Thus the single infrared $\nu(\text{CO})$ frequency pattern of $\text{Cr}(\text{CO})_6$ was converted to the characteristic three $\nu(\text{CO})$ frequency pattern characteristic of a C_{4v} $\text{LCr}(\text{CO})_5$ derivative with the concurrent production of 1.3 mmol CO/mmol of $\text{Cr}(\text{CO})_6$ (Fig. 9). When the light was turned off the $\text{LCr}(\text{CO})_5$ slowly reacted with the CO in the atmosphere above the reaction solution to

regenerate $\text{Cr}(\text{CO})_6$ as indicated by reappearance of its characteristic single $\nu(\text{CO})$ frequency. This process could be repeated. When sodium formate was added to this solution at the 60°C reaction temperature and the irradiation was continued, production of H_2 was observed. The production of H_2 could be stopped by turning off the heat (Fig. 9).

These experimental observations suggest that the mechanism discussed above for the water gas shift reaction with an $\text{M}(\text{CO})_6$ catalyst precursor (Figs. 6 and 7) also applies to the photolytic generation of H_2 from formate in the presence of $\text{Cr}(\text{CO})_6$. The essential features of this mechanism can be reduced to the following equations:



Here Eq. (12c) represents the combined results of the rate-determining decarboxylation step (see Eq. (6b)) and the subsequent fast hydrolysis and dehydrogenation reactions (see Eqs. (6c) and (6d)). Since the concentration of water far exceeds that of $\text{HCr}(\text{CO})_5^-$ and the H_2 (or HCO_3^-) produced, the decarboxylation reaction (Eq. (6b)) can be considered to be pseudo-first-order in $[\text{HCO}_2\text{Cr}(\text{CO})_5]^-$.

The steady-state approximation may be applied to Eqs. (12a–c) to yield the following rate expressions for H_2 production:

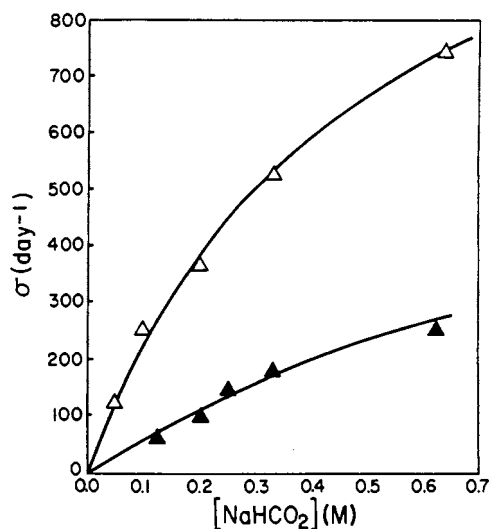


Fig. 8. Plot of the rate of H_2 production expressed as turnover number, $\sigma = \text{mol H}_2/\text{mol Cr}(\text{CO})_6$ per day, shown plotted as a function of the molar concentration of sodium formate. Catalysts solutions: $\text{Cr}(\text{CO})_6$ (0.14 mmol), pyridine (mmol): $\triangle = 0.00$, $\blacktriangle = 0.80$; 40 ml of 95% aqueous methanol under argon ($P_{\text{Ar}} = 1$ atm), $T = 60 \pm 0.5^\circ\text{C}$; the source of illumination was a Westinghouse 100 W mercury spotlight.

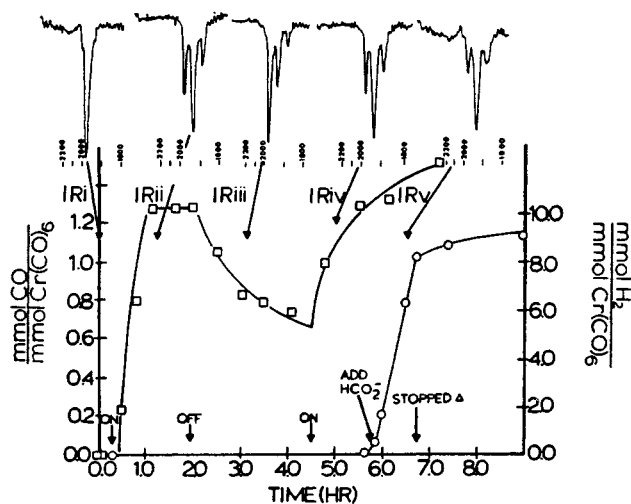


Fig. 9. Infrared spectra and gas phase composition measurements taken concurrently with a catalyst solution: $\text{Cr}(\text{CO})_6$ (0.20 mmol), NaHCO_2 (8 mmol), 40 ml of 95% aqueous methanol under N_2 ($P_{\text{N}_2} = 1 \text{ atm}$), $T = 60 \pm 0.5^\circ\text{C}$. Infrared spectra in the $\nu(\text{CO})$ region of small (1 ml) samples removed from the catalyst solution taken as a function of time are shown at the top of this Figure. The five arrows below each spectrum indicate the times at which these samples were taken. The three arrows at lower left mark the times at which illumination was begun or terminated. The two arrows at lower right indicate the times at which sodium formate was added and heating (Δ) was stopped. The lower curves show the quantities of CO (\square expressed as mmol CO present/mmol $\text{Cr}(\text{CO})_6$ initially present: left ordinate) and H_2 (\circ expressed as mmol H_2 produced/mmol $\text{Cr}(\text{CO})_6$ initially present: right ordinate) plotted as a function of time.

$$\text{Rate} = \frac{d[\text{H}_2]}{dt} = \frac{k'_3[\text{Cr}]_0[\text{HCO}_2^-]}{K_M + [\text{HCO}_2^-]} \quad (13)$$

In Eq. (13);

$$[\text{Cr}]_0 \approx [\text{Cr}(\text{CO})_5] + [\text{HCO}_2\text{Cr}(\text{CO})_5]^- \quad (14a)$$

$$k'_3 = k_3[\text{H}_2\text{O}] \quad (14b)$$

$$K_M = \frac{k_{-2} + k'_3}{k_2} \quad (14c)$$

Eq. (13) has the same functional form as the Michaelis–Menten equation. Therefore, it is convenient to rewrite Eq. (13) in reciprocal form while expressing the rate of H_2 production as turnover numbers

$$\sigma = \frac{1}{[\text{Cr}]_0} \cdot \frac{d[\text{H}_2]}{dt} \quad (15)$$

to yield:

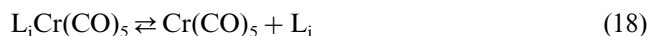
$$\frac{1}{\sigma} = \frac{1}{k'_3} + \frac{K_M}{k'_3} \cdot \frac{1}{[\text{HCO}_2^-]} \quad (16)$$

Our kinetic data for the simple decomposition of formate ion using 0.14 mmol $\text{Cr}(\text{CO})_6$ in 40 ml of 95% aqueous CH_3OH plotted in the double reciprocal form (σ^{-1} versus $[\text{HCO}_2^-]^{-1}$) were found to describe a

straight line having a slope and intercept of $3.6 \times 10^{-4} \text{ M day}^{-1}$ and $0.83 \times 10^{-3} \text{ day}$, respectively. According to Eq. (16) these values correspond to a maximum turnover number of $k'_3 = 1.2 \times 10^3 \text{ day}^{-1}$ for the decomposition of $\text{HCO}_2\text{Cr}(\text{CO})_5^-$ and a value of $K_M = 0.43 \text{ M}$ at 60°C . The data from a similar experiment with 0.80 mmol of added pyridine were also found to describe a straight line which shared a common intercept with the kinetic data measured in the absence of pyridine. The slope of the line fit to these latter data is $1.9 \times 10^{-3} \text{ M}^{-1} \text{ day}$. This is the behavior expected for competitive inhibition and therefore suggests that pyridine acts as an inhibitor by competing with the substrate, namely formate ion, for the catalytically active Cr compound that binds with formate ion in the step in which formate ion is taken into the catalytic cycle. According to the mechanism proposed here, this must occur in Eq. (12a) with pyridine competing with HCO_2^- for solvated $\text{Cr}(\text{CO})_5$. Assuming that this mechanism for competitive inhibition by pyridine is correct, Eq. (16) can easily be shown to take the following form in the presence of an inhibitor, L_i :

$$\frac{1}{\sigma} = \frac{1}{k'_3} + \frac{K_M}{k'_3} \left(1 + \frac{[\text{L}_i]}{K_{\text{L}_i}} \right) \frac{1}{[\text{HCO}_2^-]} \quad (17)$$

Here $[\text{L}_i]$ denotes the molar concentration of the inhibitor ligand and K_{L_i} denotes the dissociation constant that governs the equilibrium:

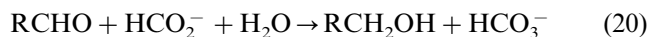


In accord with Eqs. (16) and (17) the ratio of the slopes of the straight lines taken in the presence and absence of pyridine is numerically equal to the term $(1 + \{[\text{L}_i]/K\})$. The concentration of pyridine in these experiments is $[\text{L}_i] = 0.80 \text{ mmol}/40 \text{ ml} = 0.02 \text{ M}$. The ratio of slopes referred to above is

$$\frac{1.9 \times 10^{-3} \text{ M day}}{3.6 \times 10^{-4} \text{ M day}} = 5.3 \quad (19)$$

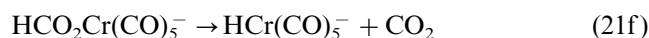
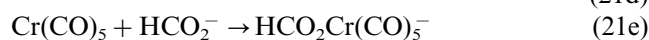
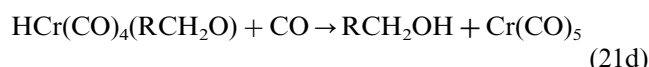
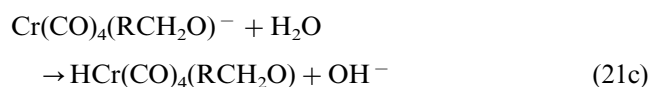
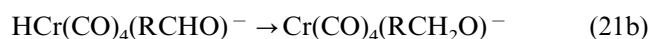
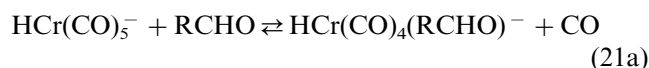
This yields a value of $K_{\text{L}_i} = 4.7 \times 10^{-3} \text{ M}$ for the reaction shown in Eq. (18). This is considerably smaller than K_M . This suggests that, to the extent that k'_3 can be neglected in comparison to k_{-2} , pyridine has a much greater affinity for $\text{Cr}(\text{CO})_5$ than the formate ion.

The photocatalytic $\text{HCO}_2^-/\text{Cr}(\text{CO})_6$ system can also be used to hydrogenate aldehydes to the corresponding alcohols by the following overall reaction (Fig. 10, [28]):



Thus the aldehydes RCHO ($\text{R} = 1\text{-heptyl}$, $p\text{-tolyl}$, and $p\text{-anisyl}$) were found to be hydrogenated to the corresponding alcohols RCH_2OH with sodium formate in aqueous methanol when photolyzed in the presence of a catalytic amount of $\text{Cr}(\text{CO})_6$. Detailed kinetic studies on the $p\text{-tolualdehyde}$ hydrogenation by this

method indicate saturation kinetics in formate ion, autoinhibition by the *p*-tolualdehyde, and a threshold effect for $\text{Cr}(\text{CO})_6$ at concentrations greater than 0.004 M. These data suggest that the presence of an aldehyde can interrupt hydrogen production by the water gas shift catalytic cycle through interception of the $\text{HCr}(\text{CO})_5^-$ intermediate by the aldehyde by the following sequence of reactions:



The aromatic aldehyde *p*-tolualdehyde was found to inhibit completely the photoproduction of H_2 by the $\text{NaHCO}_2/\text{Cr}(\text{CO})_6/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ system (Fig. 10, bottom) whereas the aliphatic aldehyde 1-heptanal was found to inhibit the photoproduction of H_2 only when the partial pressure of H_2 over the system reached 0.5 to 1.0 atm (Fig. 10).

6. Noble metal-catalyzed reactions arising from the formic acid pretreatment of simulated nuclear waste media

The work outlined above on carbon monoxide and formate reactions catalyzed by metal carbonyl systems was completed by the late 1980s. Subsequently, during the summers of 1989 and 1990 I worked at the Westinghouse Savannah River Technical Center near Aiken, South Carolina, as a summer faculty research participant exploring various applications of inorganic chemistry to environmental problems associated with the disposal of highly radioactive nuclear wastes currently located in 'tank farms' at the Savannah River and Hanford nuclear sites. In this connection the most promising method for such disposal appears to be a vitrification process in which the nuclear wastes are incorporated into borosilicate glass, the molten glass is poured into large stainless steel canisters, and the sealed canisters are buried in suitably protected burial sites (Fig. 11).

Operation of a glass melter and durability of the glass is affected by the redox state of the glass during processing. Formation of a conductive metallic sludge

in an overreduced melt can result in a shortened melter lifetime. An overoxidized melt may lead to foaming and loss of ruthenium as volatile RuO_4 . Historically, foaming in the melter has been controlled by introduction of a reductant into the melter feed. For this reason formic acid was selected by the Savannah River site for its nuclear waste vitrification plant since it is an acid that

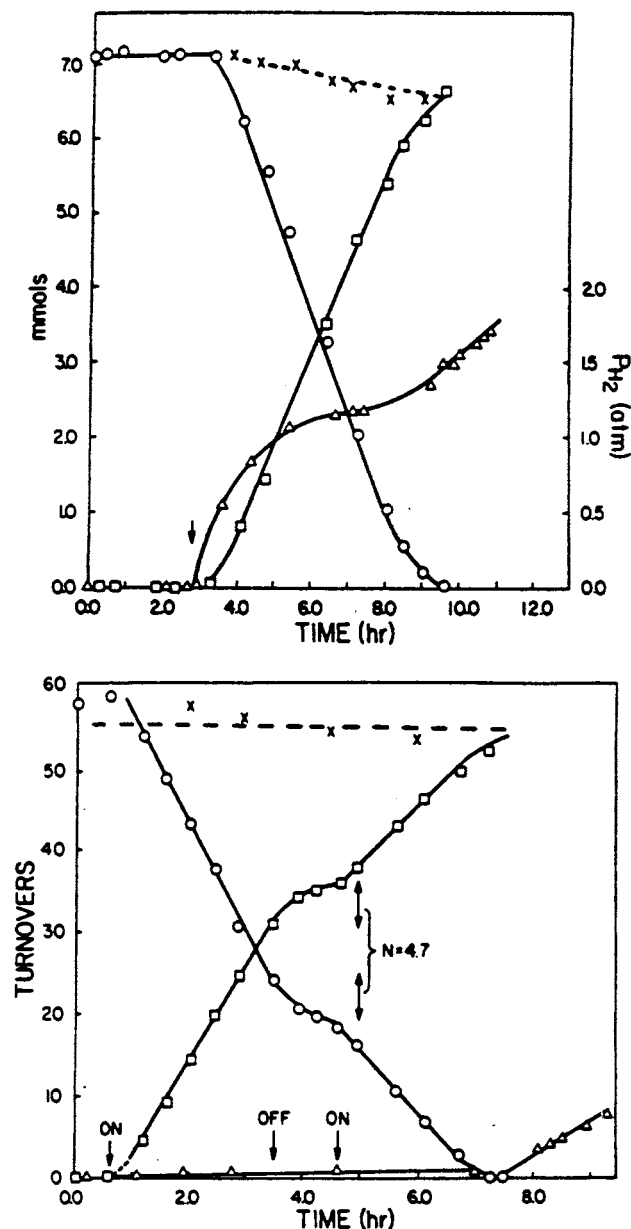


Fig. 10. Hydrogenations of 1-heptanal (top) and *p*-tolualdehyde (bottom) using $\text{Cr}(\text{CO})_6$ (0.134 ± 0.014 mmol), NaHCO_2 (13 mmol), and aldehyde (7.9 ± 0.7 mmol) in 40 ml 95% aqueous methanol under 1 atm argon, temperature $60 \pm 0.5^\circ\text{C}$. The plots depict aldehyde consumed (\circ), alcohol produced (\square), and H_2 produced (\triangle) as functions of time. The arrows indicate the times at which the Westinghouse 100 W mercury spotlight used to illuminate the solution was turned ON or turned OFF.

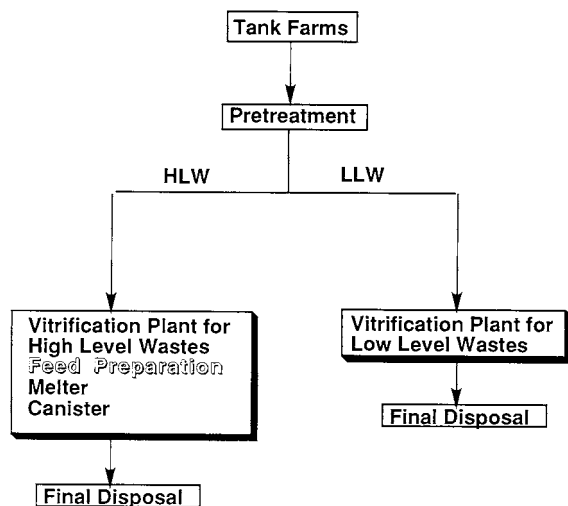


Fig. 11. Flow chart proposed for treatment of nuclear wastes at the Hanford site (1994).

not only solubilizes the metals but also reduces Hg^{2+} and Hg_2^{2+} to mercury metal and manganese in MnO_2 to Mn^{2+} . Formic acid also decreases the melter feed viscosity thereby reducing the pumping needs for the plant.

For these reasons, starting in the late 1980s laboratory- and pilot-scale studies were carried out both at the Savannah River and Hanford nuclear sites using formic acid for the pretreatment of simulated nuclear wastes. However, in 1988, H_2 generation was observed in work in the Pacific Northwest National Laboratory at the Hanford site during treatment of simulated high level waste with formic acid in a laboratory-scale apparatus [29]. Subsequent pilot-scale studies at the Savannah River site in 1990 confirmed H_2 generation during the formic acid pretreatment of simulated nuclear wastes leading to levels of H_2 as high as three to four times its flammability limit, thereby creating some concern about the safety of the formic acid pretreatment of nuclear wastes prior to their vitrification. Because of the concern at the Savannah River site about this issue, I was called in fall 1990 to be a consultant to assist them in finding the cause of this unwanted H_2 generation and developing methods for its reduction or elimination. This interest in the part of the Savannah River and Hanford nuclear sites eventually led to research contracts from both sites to study this issue in some depth at The University of Georgia during the period 1991–1994. Within the first few months of this work, which was initially supported by the Savannah River site, it became apparent that a homogeneous catalytic process involving nitrorhodium complexes generated from the rhodium produced in uranium fission and nitrite added as a corrosion inhibitor played a key role in the H_2 generation from formic acid [30].

Subsequent work, supported during the period 1992–1994 by the Pacific Northwest National Laboratory at the Hanford site, led to a more detailed understanding of this and related processes.

The bulk of this research used feed simulants prepared on a 1-l scale from reagent grade chemicals using the protocol summarized in Fig. 12. Samples of these feed simulants (generally 40–50 ml) were treated with 88 wt.% formic acid in a 550 ml closed glass reactor at 80–100°C. The formic acid was added at this reaction temperature at a constant rate using 10 ml plastic disposable syringes driven by a Sage Instruments syringe pump (model 355). The standard rate of addition of formic acid corresponded to 0.448 mmol $\text{HCO}_2\text{H}/\text{min}$ or 26.9 mmol $\text{HCO}_2\text{H}/\text{h}$. The composition of the gas phase was analyzed periodically for H_2 , CO_2 , NO , and N_2O using the same gas chromatography equipment as used earlier for the work on the water gas shift reaction.

Initial studies at the University of Georgia screened the four noble metals found in uranium fission products, namely Ru, Rh, Pd, and Ag, for their catalytic activity for the decomposition of pure formic acid [31]. Subsequent studies [30] investigated the catalytic activities of these noble metals for formic acid decomposition in the feed simulants. Other components in these simulants, notably NO_2^- , were found to modify profoundly the catalytic activity of the noble metals of interest for formic acid decomposition. The most active catalyst precursor for H_2 evolution from the simulant was found to be $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, even though it was inactive as a catalyst precursor for H_2 evolution from pure formic acid at the same temperature. Effects of changing the Rh source, Rh concentration, NO_2^- concentration, and temperature on the nitrite-promoted Rh-catalyzed formic acid decomposition in nuclear waste feed simulant media (Fig. 12) have been examined [32,33].

Fig. 13 illustrates a titration of 50 ml of the standard feed simulant (Fig. 12) with 88 wt.% formic acid at 90°C in the presence of 14 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ as a soluble Rh catalyst precursor. Production of H_2 began only after all of the CO_3^{2-} has been converted to CO_2 and the NO_2^- to NO and N_2O . This immediately suggests that one method of limiting H_2 production during the treatment of nuclear wastes with formic acid is to limit the amount of formic acid to that required to convert all of the CO_3^{2-} to CO_2 and the NO_2^- to NO and N_2O . A total of 1.3 mmol of H_2 was produced in this experiment.

Insoluble Rh sources rather than soluble $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ were also investigated as catalyst precursors. Two rather different methods of introducing Rh in an insoluble form were investigated. In the first method, Rh was introduced into the feed simulant as hydrous Rh_2O_3 by coprecipitation in the iron fraction

(Fig. 12) using hydrated $\text{Rh}(\text{NO}_3)_3$ as the Rh source at a concentration of 0.28 g l^{-1} . Titration of 50 ml of this feed simulant with 85 mmol of formic acid at $88 \pm 2^\circ\text{C}$ led to the production of a total of 1.4 mmol of H_2 as compared with 1.3 mmol of H_2 in a comparable experiment in which Rh was introduced as the soluble $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. No significant differences were observed in the behavior of this system when Rh was coprecipitated with the other metal oxides in the feed simulant preparation as compared with otherwise similar experiments in which $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ is added to the slurry immediately before the start of the experiment.

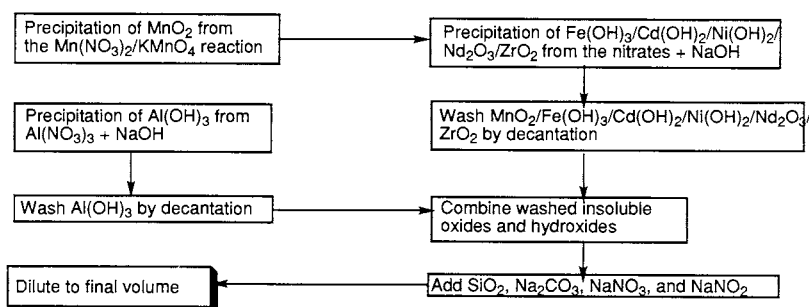
In the second method, Rh was introduced as a 5% dispersion of the metal supported on carbon or alumina using 0.1175 g of 5% Rh/C or 0.115 g of 5% Rh/ Al_2O_3 , respectively, corresponding to the amount of Rh in the 14 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ used in the standard experiments. The observed behavior with these solid 5% Rh dispersions in the standard feed simulant upon titration with 85 mmol of 88 wt.% formic acid at 90°C was very different from the observed behavior with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in the following ways:

(1) Only a very small amount of H_2 was produced (0.16 mmol and 0.28 mmol at the end of the experiments with 5% Rh/C and 5% Rh/ Al_2O_3 , respectively).

(2) The initially produced NO but not the N_2O was almost entirely consumed during the course of the experiment. For example, a maximum of 9.29 mmol of NO was measured after 216 min but only 1.25 mmol of NO remained at the end of the experiment with 5% Rh/C.

The drastically reduced production of H_2 and the consumption of NO as the reaction proceeds suggests that Rh dispersed on carbon might be an active catalyst for the hydrogenation of NO. This is supported by the production of a relatively large amount of CO_2 in this experiment as well as by studies on ammonia formation reported elsewhere [33,34].

A series of six experiments was performed in which 50 ml samples of the standard feed simulant and 10 ml of water each were titrated at 91°C with a total of 86 mmoles of formic acid in the presence of amounts of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ranging from 1.4 mg (0.0056 mmol) to 14 mg (0.056 mmol) in an attempt to assess the minimum amount of Rh needed to catalyze H_2 evolution from formic acid. Generation of H_2 was found to occur after sufficient formic acid had been added to deplete the NO_2^- and CO_3^{2-} . The maximum rate of H_2 production was found to be pseudo first-order in Rh concentration (mol l^{-1}) according to the following equation:



Sources of the Components of the Feed Simulant UGA-12M1

Component	Molarity	Source	g/liter	Water solubility
Al	0.226	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	84.8 g	63.7 g/100g @ 25°C
Cd	0.03	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	9.2 g	215 g/100 g @ 25°C
Fe	0.45	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	181.8 g	"soluble"
Mn	0.0314	{ KMnO_4 $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	{ 2.0 g 5.4 g	{ 6.38 g/100 g @ 20°C 426.4 g/100 g @ 0°C
Nd	0.0264	$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	11.6 g	152.9 g/100 g @ 25°C
Ni	0.0392	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	11.6 g	238.5 g/100 g @ 0°C
Si	0.0854	SiO_2	5.1 g	insoluble
Zr	0.156	$\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	52.9 g	soluble
Na^+	0.801	$\text{Na}_2\text{CO}_3 +$ $\text{NaNO}_3 + \text{NaNO}_2$	see below	see below
CO_3^{2-}	0.125	Na_2CO_3	13.2 g	7.1 g/100 g @ 0°C
NO_3^-	0.116	NaNO_3	9.9 g	92.1 g/100g @ 25°C
NO_2^-	0.435	NaNO_2	30.0 g	81.5 g/100 g @ 15°C

Fig. 12. Preparation of the non-radioactive nuclear waste feed simulant used in this work.

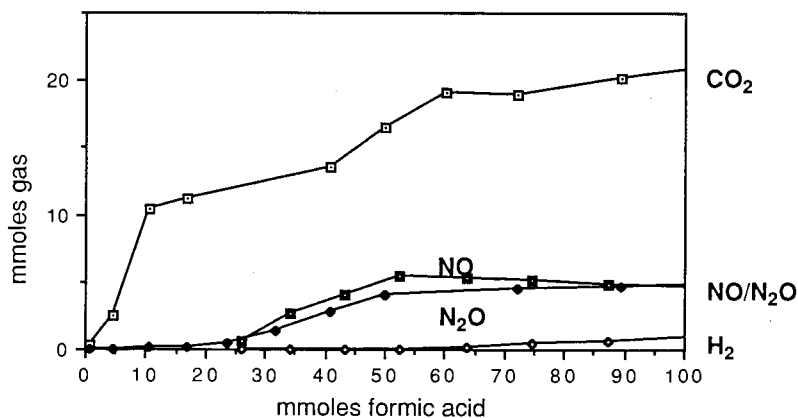


Fig. 13. Gas generation upon titration of 50 ml of the feed simulant with 88% formic acid at a rate of $0.0196 \text{ ml min}^{-1} = 0.42 \text{ mmol min}^{-1}$ in the presence of 14 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ at 90°C .

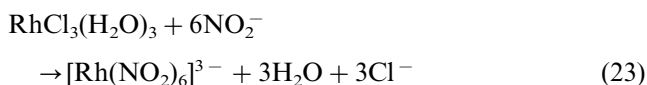
$$\text{H}_2 \text{ production (mmol min}^{-1}\text{)} = -0.92 + 8030 [\text{Rh}]$$

$$R^2 = 0.952 \quad (22)$$

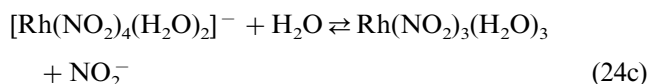
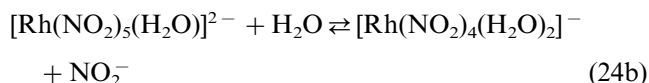
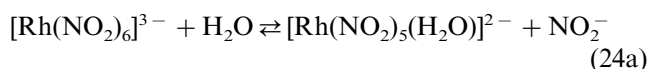
Since NO_2^- has been shown to promote the catalytic activity of Rh for formic acid decomposition in feed simulant media, it was of interest to investigate the effect of NO_2^- concentration on the reaction rate. A series of four experiments involving titration of 50 ml of a nitrite-free feed simulant, 14 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, 10 ml of water, and amounts of NaNO_2 ranging from 0.6 to 1.5 g in 0.3-g increments with 85 mmol of formic acid indicated that the rate of H_2 production is relatively insensitive to NO_2^- concentration at relatively high NO_2^- concentrations. The expected production of NO and N_2O was observed in all of the experiments. There were no major qualitative differences, and the amounts of nitrogen oxides appeared roughly proportional to the amount of NaNO_2 used.

The role of the NO_2^- ion as a promoter suggests the role of soluble nitrorhodium complexes as intermediates in the Rh-catalyzed decomposition of formic acid. In this connection, RhCl_3 was reported more than a century ago [35] to react with excess NO_2^- in boiling water to give salts of the hexanitrorhodate anion, $[\text{Rh}(\text{NO}_2)_6]^{3-}$. Three of the six nitro groups in $[\text{Rh}(\text{NO}_2)_6]^{3-}$ are reported to be labile upon treatment with strong oxidants [36] or sulfamic acid [37] indicating the feasibility of opening catalytic sites on the central Rh atom under the conditions of formic acid decomposition. These vacant sites on the central Rh atom can be used both for anchoring onto an insoluble hydrous oxide support as well as for coordination with formic acid prior to its decomposition.

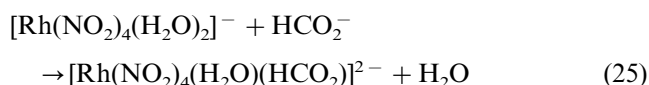
The reaction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with NO_2^- to give $[\text{Rh}(\text{NO}_2)_6]^{3-}$ can be summarized by the following equation:



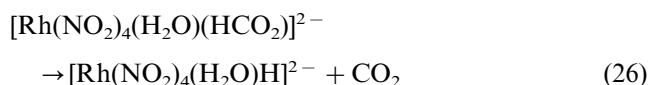
The lability of three of the six nitro groups in $[\text{Rh}(\text{NO}_2)_6]^{3-}$ can be summarized by the following equations in which nitro groups are successively replaced by more labile aquo ligands:



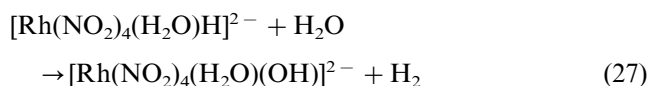
Formate can then displace the aquo ligands by reactions such as the following:



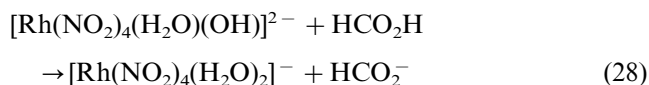
Coordinated formate can undergo a hydrogen shift from carbon to a vacant rhodium site with carbon dioxide evolution to generate a rhodium hydride according to the following equation:



Hydrolysis of the rhodium hydride, possibly acid catalyzed, can then result in the observed hydrogen evolution, i.e.



The resulting hydroxorhodium complex can then be protonated by formic acid to regenerate the original diaquo derivative, i.e.



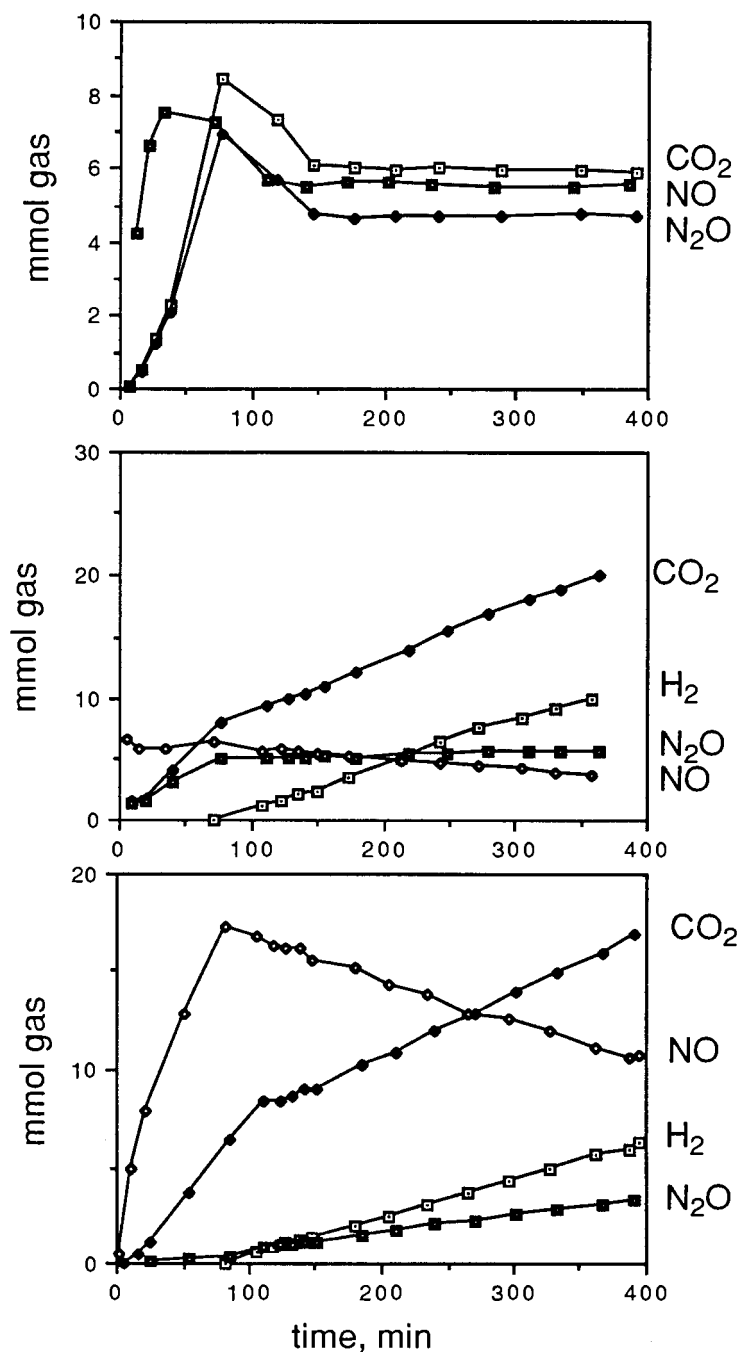


Fig. 14. Titration of 1.5 g of NaNO_2 in 60 ml of water with 88 wt.% formic acid at 90°C in the absence of added metals (top), in the presence of 14 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (middle), and in the presence of 14 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and 100 mg CuCl_2 (bottom).

The net sum of Eqs. (25)–(28) is the observed formic acid decomposition



In this mechanistic scheme, NO_2^- is essential to the reaction but excess NO_2^- can inhibit the reaction by tying up catalytic sites forming $[\text{Rh}(\text{NO}_2)_6]^{3-}$ (see Eq. (24a)). The balance between the requirement of NO_2^- to make active nitrorhodium intermediates but the ability of excess NO_2^- to inhibit the reaction can account

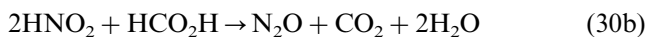
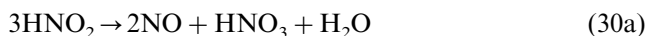
for the observed insensitivity of the reaction rate to NO_2^- concentration.

The mechanism suggested above (Eqs. (23)–(28)) for the nitrorhodium catalyzed decomposition of formic acid to $\text{CO}_2 + \text{H}_2$ bears a close resemblance to the mechanism of the water gas shift reaction catalyzed by tungsten carbonyls (Eqs. (5)–(7)) except that the CO ligands attached to the low-valent W(0) are replaced by NO_2 groups in the corresponding Rh(III) complexes. Note that W(0) and Rh(III) are both d^6 metals so that

these two catalyst systems may be regarded as isoelectronic.

Some limited component studies were performed on formic acid decomposition catalyzed by nitrorhodium complexes. The objective of these studies was to simplify the complicated nuclear waste simulants to the minimum number of components required to catalyze formic acid decomposition under the observed conditions. In this connection the required components for such studies were limited to Rh(III) as the noble metal catalyst and nitrite as an ancillary ligand. In some experiments Cu(II) was added with the original idea of improving catalyst life by inhibiting reduction of soluble rhodium complexes to rhodium metal.

The results of the limited component experiments are summarized in Fig. 14. The titration of NaNO₂ with formic acid at 90°C in the absence of any metals (Fig. 14, top) leads to the production of CO₂, NO, and N₂O from the reactions of the nitrous acid generated upon acidification of nitrite ion according to the following equations:

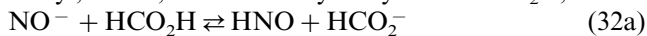


This pattern of CO₂, NO, and N₂O production can be taken as a 'signature' for nitrous acid generated by acidification of nitrite with formic acid. Addition of a small amount of RhCl₃·3H₂O to the reaction mixture before initiating the formic acid titration has relatively little effect on the composition of the gas phase during the period where nitrous acid is generated and subsequently decomposes. However, H₂ is generated by further addition of formic acid after the initial generation and decomposition of nitrous acid is complete (Fig. 14, middle).

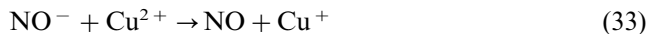
The addition of Cu(II) as a soluble salt to the nitrite/Rh(III) mixture before titration with formic acid has an interesting effect on the N₂O/NO ratio by drastically increasing the amount of NO relative to N₂O (e.g. Fig. 14, bottom). The initial deoxygenation product of nitrite by formic acid is expected to be the unstable NO⁻ anion formed by the following reaction:



In the absence of Cu(II) the NO⁻ anion can be protonated with formic acid to give the unstable nitroxyl, HNO, which readily dehydrates to H₂O, i.e.



However, if Cu(II) is present, it can intercept the NO⁻ by oxidation to neutral NO through a single electron transfer process, i.e.



The reaction can be made catalytic in copper by reoxidizing the Cu⁺ to Cu²⁺ with nitrous acid thereby also generating more NO, i.e.



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References

- [1] R.B. King, *J. Organometal. Chem.* 100 (1975) 111.
- [2] R.R. Hautala, R.B. King, C. Kotal, in: R.R. Hautala, R.B. King, C. Kotal Jr. (Eds.), *Solar Energy: Chemical Conversion and Storage*, Humana Press, Clifton, NJ, 1979, pp. 333–369.
- [3] R.B. King, A.D. King Jr., D.B. Yang, *ACS Symposium Series* 152 (1981) 123.
- [4] G. Pályi, R.B. King, *Inorg. Chim. Acta* 15 (1975) L23.
- [5] R.B. King, *Accts. Chem. Res.* 5 (1972) 177.
- [6] R.B. King, J. Bakos, C.D. Hoff, L. Markó, *J. Org. Chem.* 44 (1979) 3095.
- [7] C. Hoff, F. Ungváry, R.B. King, L. Markó, *J. Am. Chem. Soc.* 107 (1985) 666.

- [8] T.M. Bockman, J.F. Garst, R.B. King, L. Markó, F. Ungváry, *J. Organometal. Chem.* 279 (1985) 165.
- [9] C.L. Thomas, *Catalytic Processes and Proven Catalysts*, Academic Press, New York, 1970.
- [10] R.M. Laine, R.C. Rinker, P.C. Ford, *J. Am. Chem. Soc.* 99 (1977) 252.
- [11] H. Kang, C.H. Mauldin, T. Cole, W. Slegier, K. Cann, R. Pettit, *J. Am. Chem. Soc.* 99 (1977) 8323.
- [12] N.S. Imyanitov, B.E. Kuvaev, D.M. Rubkovskii, *Zhur. Prikl. Khim.* 49 (1967) 2821.
- [13] R.B. King, A.D. King Jr., *Russ. Chem. Bull.* 43 (1994) 1445.
- [14] C.-H. Cheng, D.E. Hendricksen, R. Eisenberg, *J. Am. Chem. Soc.* 99 (1977) 8323.
- [15] C.-H. Cheng, R. Eisenberg, *J. Am. Chem. Soc.* 100 (1978) 5968.
- [16] T. Yoshida, Y. Ueda, S. Otsuka, *J. Am. Chem. Soc.* 100 (1978) 3941.
- [17] R.B. King, C.C. Frazier, R.M. Hanes, A.D. King Jr., *J. Am. Chem. Soc.* 100 (1978) 2925.
- [18] A.D. King Jr., R.B. King, D.B. Yang, *J. Am. Chem. Soc.* 102 (1980) 1028.
- [19] A.D. King Jr., R.B. King, D.B. Yang, *J. Am. Chem. Soc.* 103 (1981) 2699.
- [20] G.J. Kubas, *Accts. Chem. Res.* 21 (1988) 120.
- [21] G.J. Kubas, R.R. Ryan, B.I. Swanson, P.J. Vergamini, H.J. Wasserman, *J. Am. Chem. Soc.* 106 (1984) 451.
- [22] A.D. King, R.B. King, D.B. Yang, *J. Chem. Soc. Chem. Comm.*, (1980) 529.
- [23] W. Reppe, H. Vetter, *Liebigs Ann. Chem.* 582 (1953) 133.
- [24] R. Massoudi, J.H. Kim, R.B. King, A.D. King Jr., *J. Am. Chem. Soc.* 109 (1987) 7428.
- [25] J. Palágyi, L. Markó, R.B. King, A.D. King Jr., unpublished results (1984–1985).
- [26] A.D. King Jr., R.B. King, E.L. Sailors III, *J. Am. Chem. Soc.* 103 (1981) 1867.
- [27] D.E. Linn Jr., R.B. King, A.D. King Jr., *J. Mol. Catal.* 80 (1993) 151.
- [28] D.E. Linn Jr., R.B. King, A.D. King Jr., *J. Mol. Catal.* 80 (1993) 165.
- [29] K.D. Wiemers, presented at the American Institute of Chemical Engineers 1988 Summer National Meeting, Denver, CO, August, 1988.
- [30] R.B. King, A.D. King Jr., N.K. Bhattacharyya, C.M. King, L.F. Landon, in: W.W. Schultz, E.P. Horwitz (Eds.), *Chemical Pretreatment of Nuclear Waste for Disposal*, Plenum Press, New York, 1995.
- [31] R.B. King, A.D. King Jr., N.K. Bhattacharyya, *Transition Metal Chem.* 20 (1995) 321.
- [32] R.B. King, N.K. Bhattacharyya, K.D. Wiemers, *Environ. Sci. Tech.* 30 (1996) 1292.
- [33] R.B. King, N.K. Bhattacharyya, H.D. Smith, K.D. Wiemers, *J. Mol. Catal.* 107 (1996) 145.
- [34] R.B. King, N.K. Bhattacharyya, H.D. Smith, K.D. Wiemers, *Environ. Sci. Tech.* 31 (1997) 984.
- [35] E. Leidić, *Compt. Rend.* 111 (1890) 106.
- [36] Yu.N. Kukushkin, O.V. Stefanova, *Russ. J. Inorg. Chem.* 22 (1977) 1844.
- [37] N.V. Mel'chakova, G.P. Ozerrova, V.M. Peshkova, *Russ. J. Inorg. Chem.* 12 (1967) 577.