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COMPARATIVE ENERGY BARRIERS FOR HYDROGEN ACTIVATION BY HOMOGENEOUS AND HETEROGENEOUS METAL OXIDE CATALYSTS * *

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Triethylene glycol solutions of alkali and alkaline earth metal hydroxide complexes are well-defined soluble oxide water-gas shift catalysts which equilibrate the reaction of carbon monoxide and water to yield hydrogen and carbon dioxide at temperatures ranging from 150° to 250°C and carbon monoxide pressures of 1 to 300 atm. Significantly, catalysis proceeds cleanly, even in the complete absence of a metal center in the soluble oxide system. Thus, the rate of hydroxide ion catalyzed hydrogen evolution is highest in the presence of a noncoordinating organic cation: $Bu_4N^+ > Cs^+ > Na^+ > H^+ > Ca^{+2}$. Furthermore, the activation energy for the homogeneous sodium hydroxide catalyst in triethylene glycol solution, 26 ± 1 kcal, is comparable to that exhibited by a commercially used heterogeneous iron oxide catalyst, 27 ± 0.2 kcal. The alkali metal hydroxide system may be modified for metal cocatalysis. Thus, lead (II) oxide dissolves in the triethylene glycol solutions to yield a new species which exhibits a ^{207}Pb NMR resonance shifted 3350 ppm downfield from lead perchlorate. The activity of this lead modified system is improved by three orders of magnitude. Yet, the activation energy is unchanged, 26 ± 1 kcal, suggesting that entropic factors may be important in these homogeneous metal oxide hydrogen evolution/activation systems.

Hydrogen activation, metal oxide, formate, water-gas shift, catalysis

1. Introduction

Hydrogen activation by metal oxide catalysts is a fundamental reaction which is central to numerous industrial processes, including: catalytic methanol synthesis, petroleum hydrocracking, and ammonia production. Furthermore, previous mechanistic studies of metal oxide systems have focused primarily on reactions

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occurring at the metal center [1]. Yet, there is ample precedent to suspect that the nucleophilic oxide ligand may be a concurrent site of reactivity [2], since hydrogen/deuterium exchange is catalyzed by aqueous solutions of sodium hydroxide [3] and lithium butoxide has been employed as a nontransition metal hydrogenation catalyst [4]. We report here the catalysis of the water-gas shift reaction with alkali metal hydroxide complexes in triethylene glycol solution, (1),

$$CO + H_2O \overset{OH^-}{\rightleftharpoons} H_2 + CO_2 \tag{1}$$

and compare the resultant activation energy for hydrogen evolution to that exhibited by industrially used heterogeneous metal oxide catalysts. The homogeneous water-gas shift system is of fundamental mechanistic interest, since it allows the reactivity of solvated hydroxide ion to be compared with that exhibited by more traditional metal oxide catalysts where the metal and the oxide centers are free to exert synergistic effects.

2. Experimental

MATERIALS

Sodium, cesium, lithium, and calcium formate were purchased from Alfa Products. Reagent grade lead (II) oxide from General Chemical Co. of New York was used without purification. Triethylene glycol, HPLC grade water, and formic acid were obtained from Aldrich. The triethylene glycol was distilled *in vacuo* immediately prior to use. Similarly, the formic acid was titrated with a standard sodium hydroxide solution before use. Matheson purity carbon monoxide was employed in all of the runs. The tetrabutylammonium formate was synthesized by reacting a 25% weight solution of tetrabutylammonium hydroxide in methanol, from Alfa Products, under 150 atm of carbon monoxide at 100 °C for eight hours. The solvent was removed *in vacuo* and the resultant solid exhibited characteristic spectra for a formate salt: IR 1604 cm^{-1}; ^{13}C NMR ($CDCl_3$, 75.57 MHz)δ 167.4 (O_2CH^-), 58.5, 23.7, 19.41, 13.3 (Bu). It was further dried *in vacuo* over P_2O_5 at 100 °C Anal. Calcd for $C_{17}H_{37}O_2N$: C, 71.02; H, 12.97; N, 4.87. Found: C, 71.41; H, 12.12; N 4.70.

BATCH REACTIONS

The reactions of carbon monoxide and water generate significant concentrations of formic acid which is corrosive to stainless steel autoclave parts. Therefore, the reactions were conducted in 300 ml Autoclave Engineer's vessels which had been gold-plated, including the: body, encapulated magnet, stirring tower components, sealing gaskets, and rupture disk to a thickness of 0.00030-in by Precision Plating Co. of Chicago, IL. Iron pentacarbonyl was not detectable by FTIR, less than 50 μm, even after 168 hours of operation at 180 °C in the gold-plated autoclave. Three separate autoclave installations were similarly plated and found to give consistent results. In addition, a 500 ml Teflon block reactor from Berghof of America was used. This latter reactor employs a Teflon to Teflon seal and no part of the solution or gas phase contacts the outer stainless steel support walls. Moreover, the macroscopic dimensions of the Teflon block eliminates the cracking and pealing problems often encountered with simple Teflon coatings applied to stainless stell autoclave equipment. The Berghof reactor was modified, however, by shortening the liquid sample tube which surrounds the thermocouple well such that the end of the thermowell was in direct contact with the solution phase. In addition, the holes in the Teflon rotor were enlarged to provide better mixing in the viscous triethylene glycol solvent. In general, the Berghof reactor was found to be, after modification, a highly recommended addition to our high pressure facilities, although it lacks the temperature and pressure capabilities accessible with the gold-plated equipment. Gas samples were analyzed by gas chromatography for hydrogen, carbon monoxide, and carbon dioxide on a 3.5-ft spherocarb column at 40, 40, and 100 ° C. Liquid samples were analyzed spectrophotometrically on a Perkin-Elmer Model 1500 FTIR for formic acid, water, and formate ion at 1724, 1654, and 1604 cm^{-1}, respectively.

STEADY-STATE REACTIONS

Steady-state hydrogen production rates were measured at one atmosphere pressure in a single pass Pyrex tube reactor with a total internal volume of 500 ml. Water addition was controlled by an ISCO model 314 high pressure syringe pump. Carbon monoxide and water vapor were preheated in a Pyrex sidearm before passing up through a fine glass frit located at the bottom of the tube reactor. Mixing within the solution phase was accomplished by the gas dispersion process. The temperature of the solution phase was directly measured by a thermocouple located in a glass thermowell and was found to be constant to within $\pm 0.5\,^{\circ}C$ for periods of up to ten hours. The composition of the exit gas phase was monitored by gas chromatography.

LEAD COCATALYSIS

Lead (II) oxide alone has no appreciable solubility in triethylene glycol solvent. However, it readily dissolves in triethylene glycol upon warming to 100 ° C in the presence of excess sodium formate. Solutions up to 0.5 M in lead are stable upon cooling to room temperature and exhibit a single ^{207}Pb NMR resonance shifted 3350 ppm downfield from an external lead perchlorate standard. These solutions were found to be effective water-gas shift catalysts with long-term stability as demonstrated for an experiment at 145 ° C in the single pass tube reactor, table 1. Consistent with the stoichiometry of (1), the ratio of hydrogen to carbon dioxide was observed to be close to unity after the temperature had equilibrated, as demonstrated in column 5 of table 1. It is noted that the ratio of hydrogen to

Table 1
Steady-state hydrogen production with a PbO/NaOH catalyst triethylene in glycol [a]

Time (min)	Temp (° C)	H_2 (mmoles hr^{-1})	CO_2 (mmoles hr^{-1})	H_2/CO_2
0	141	0.122	0.154	0.79
30	142	0.153	0.176	0.87
60	143	0.154	0.176	0.88
105	145	0.183	0.175	1.05
340	145	0.169	0.187	0.90
400	145	0.177	0.180	0.98
1050	144	0.178	0.179	0.99
1120	145	0.178	0.181	0.98

[a] Composition of the exit gas phase at selected time intervals for the reaction of carbon monoxide at 112 mmoles hr^{-1} (0.72 atm) and water at 44 mmoles hr^{-1} (0.28 atm) through a solution phase consisting of sodium formate, 0.1 M, and lead (II) oxide, 0.01 M, in 200 ml of triethylene glycol at 145 ° C. One turnover with respect to lead corresponds to roughly 660 min at this temperature.

carbon dioxide was less than unity during periods when the temperature was increasing, as indicated in the first three rows of table 1. Dilute catalyst solutions were employed with the lead cocatalyst to keep the single pass conversions below 30%, thus minimizing the effect of back reaction on the measured rate of hydrogen evolution. The homogeneous metal oxide catalysts were characterized in units typically employed for heterogeneous metal oxide catalysts; moles of hydrogen hr^{-1} per kg of metal oxide catalyst. The weight of the solvent was not included in the comparison and would represent a significant difference in a practical application, although it has no effect on the calculation of the activation energy.

3. Results

The reaction of carbon monoxide and water in the presence of a solution of sodium formate dissolved in triethylene glycol results in the smooth evolution of hydrogen and carbon dioxide, as demonstrated in fig. 1. Formic acid is a side product obtained by the carbonylation of hydroxide ion [5], (2) and (3).

$$OH^- + CO \rightleftharpoons HCO_2^- \qquad (2)$$

$$HCO_2^- + H_2O \rightleftharpoons H_2CO_2 + OH^- \qquad (3)$$

Kinetic measurements were performed on this system by the method of initial rates on gas samples periodically removed from the autoclave experiments to yield hydrogen partial pressure vs. time plots which were linear for an eight-hour period. Furthermore, since the alkali metal hydroxide system under investigation lacks energetically accessible d-orbitals, which are usually considered important

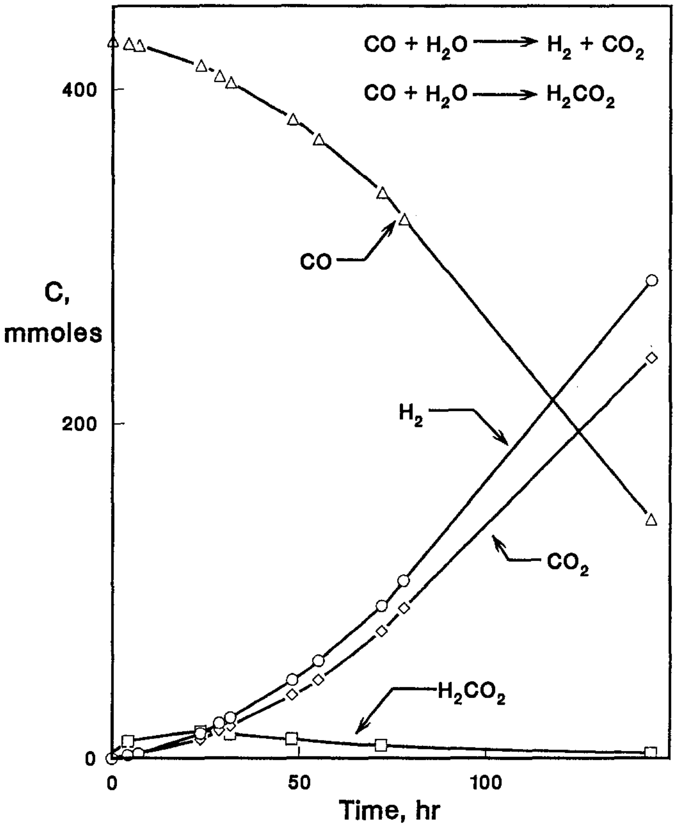

Fig. 1. Time dependence of the products in the reaction of carbon monoxide, 180 atm, and water, 7.8 M, in triethylene glycol at 180 ° C with a sodium formate catalyst, 0.1 M.

for facile hydrogen activation [1], considerable attention was devoted to background experiments designed to eliminate the possibility of surface reactions occurring on the gold-plating or cocatalysis due to trace iron contamination. The results in the first three rows of table 2 demonstrate the reproducibility of the hydrogen evolution rate measurements obtained with three different autoclave installations, all similarly gold-plated. A Pyrex liner was employed, fourth row, to reduce the surface area of the gold which is in contact with the solution phase with no measurable difference in the rate of hydrogen production. Similarly, consistent hydrogen evolution rate data were obtained in the Teflon reactor which has no exposed metal parts, in rows 5 and 6 of table 2. In addition, the 50-fold increase in the rate of hydrogen evolution noted in column 3 of table 3 varies in near direct proportion to the sodium formate concentration (activity coefficients are unavailable). The effective first order catalyst turnover frequency is tabulated in column 4 of table 3. Taken together, these observations argue against surface reactions in the system.

Table 2
Reproducibility of the initial rate of hydrogen production with a sodium formate catalyst [a]

Reactor	Temp (°C)	HCO_2Na (M)	H_2^b (mmoles hr^{-1})
Gold-plated$_1$	180	0.1	0.25
Gold-plated$_2$	180	0.1	0.25
Gold-plated$_3$	180	0.1	0.22
Glass liner	180	0.1	0.26
Teflon block	180	0.1	0.22
Teflon block	180	0.1	0.22
Stainless steel [c]	150	0.1	0.04
$Fe(CO)_5$ added [d]	180	0.1	0.18
Gold-plated$_1$	180	0.0	0.01

[a] For reaction of carbon monoxide, 180 atm, and water, 7.8 M, in triethylene glycol.

[b] Initial rate of hydrogen production from hydrogen partial pressure vs. time plots over an eight-hour period.

[c] Iron pentacarbonyl was detected within the solution phase.

[d] Iron pentacarbonyl at 1.9×10^{-3} M and formic acid at 0.14 M were added to a reaction in a gold-plate autoclave.

A second experimental consideration was the possibility of cocatalysis by adventitious sources of ion pentacarbonyl which is potentially present at concentration levels below the FTIR detection limit, 50 μm. Indeed, iron pentacarbonyl is known to be a water-gas shift catalyst in basic solution [5a,6]. However, such a mechanistic pathway should be strongly inhibited by the formic acid levels evident in fig. 1. This latter point was established by adding iron pentacarbonyl at forty times the FTIR detection limit to a solution which was

Table 3
Independence of the effective catalyst turnover frequency with sodium formate concentration [a]

$[NaO_2CH]$ (M)	$[H_2CO_2]_{avg}^b$ (M)	$(\Delta H_2/\Delta t)/Vol$ [c] (mM hr^{-1})	$\tau = (\Delta H_2/\Delta t)/Vol \cdot [NaO_2CH]$ (hr^{-1})
0.01	[d]	0.32	0.032
0.02	0.078	0.75	0.038
0.04	0.13	1.9	0.048
0.1	0.17	3.5	0.035
0.5	0.17	10.5	0.21
1.0	0.14	18.0	0.018

[a] For reaction of carbon monoxide, 180 atm, and water, 7.8 M, in triethylene glycol at 182° C.

[b] Average formic acid concentration which was produced during the first eight-hour period.

[c] Initial rate of hydrogen production from hydrogen partial pressure vs. time plots over an eight-hours period ratioed against the solution volume to give an effective concentration unit.

[d] Not detected.

Table 4
Effect of formic acid on the rate of hydrogen production with a sodium formate catalyst [a]

$[NaO_2CH]$ (M)	$[H_2CO_2]_i$ [b] (M)	$[H_2CO_2]_{avg}$ [c] (M)	$(\Delta H_2/\Delta t)$ [d] (mmoles hr^{-1})
0.1	0	0.17	0.25
0.1	0.17	0.21	0.29
0.1	0.50	0.59	0.64
0.1	1.40	1.50	1.00

[a] For reaction of carbon monoxide, 180 atm, and water, 7.8 M, in triethylene glycol at 180 ° C.

[b] Concentration of formic acid loaded into the autoclave.

[c] Average formic acid concentration during the first eight-hour period.

[d] Initial rate of hydrogen production from hydrogen partial pressure vs. time plots over an eight-hour period.

0.14 M in formic acid and 0.10 M in sodium formate. The resultant rate of hydrogen evolution in row eight of table 2 was not significantly different from that which was observed in the absence of added iron pentacarbonyl, rows 1–6 of table 2. Additional evidence against iron cocatalysis results from the pH dependence of the sodium hydroxide/formate system. Thus, the addition of formic acid over the concentration range 0.1 to 1.5 M is observed to have a beneficial effect on the rate of hydrogen production, as demonstrated in table 4. In contrast, the opposite pH trend is reported for the iron pentacarbonyl catalyzed water-gas shift system [5a,6]. Lastly, it is noted that the steady-state hydrogen production experiments were conducted at one atmosphere pressure in an all Pyrex tube reactor where adventitious contamination by iron pentacarbonyl is far less of an experimental concern than in high pressure autoclave equipment.

4. Discussion

The soluble oxide water-gas shift reaction of (1) is first order in formate ion over the concentration range, 0.01 M to 1.0 M, as demonstrated in table 3. Furthermore, the rate of hydrogen evolution at constant formate ion concentration increases with the acidity of the solution as indicated in table 4 and, therefore, argues against a bimolecular reaction involving hydroxide ion such as the Cannizzaro adduct of (4).

$$HCO_2^- + OH^- \rightleftharpoons HC(OH)(O)_2^{2-} \qquad (4)$$

Thus, it is proposed that the rate-limiting step of the soluble oxide water-gas shift reaction proceeds by hydride transfer from formate anion to a proton source, as indicated for water in (5).

$$O_2C - H^- + H^{\delta +} - OH \rightarrow CO_2 + H_2 + OH^- \qquad (5)$$

The reactions in (2) and (5) complete a closed catalytic cycle based on hydroxide ion for hydrogen production, according to (1). Current mechanistic considerations for the hydride transfer step of (5) include a concerted reaction with a four-center transition state and, alternatively, an H_3O^- ion intermediate, according to (6) and (7).

$$O_2CH^- + H_2O \rightarrow CO_2 + H_3O^- \tag{6}$$

$$H_3O^- \rightleftharpoons OH^- + H_2 \tag{7}$$

The proposed H_3O^- ion has been previously detected [7] and the reaction of hydrogen with hydroxide ion to produce H_3O^- ion (7) has been calculated to be thermodynamically favorable [8] by 16 kcals in the gas phase.

The most notable feature of the homogeneous water-gas shift reaction in (1) is that catalysis proceeds in the complete absence of a metal center, as demonstrated by using the organic cation tetrabutylammonium ion. Indeed, of all the systems in fig. 2, the metal free tetrabutylammonium system is the most active:

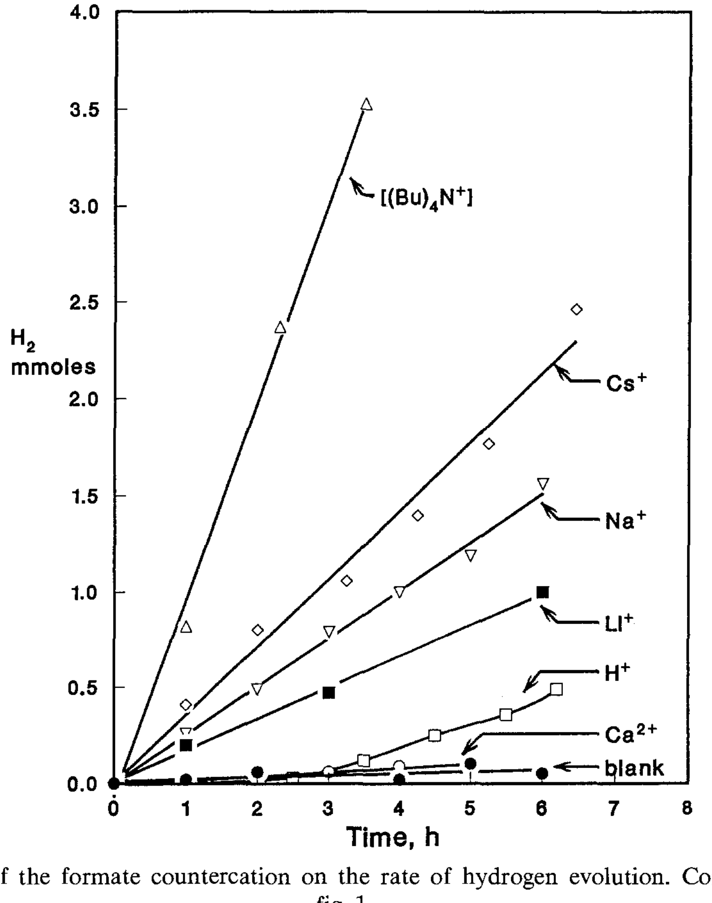

Fig. 2. Effect of the formate countercation on the rate of hydrogen evolution. Conditions as in fig. 1.

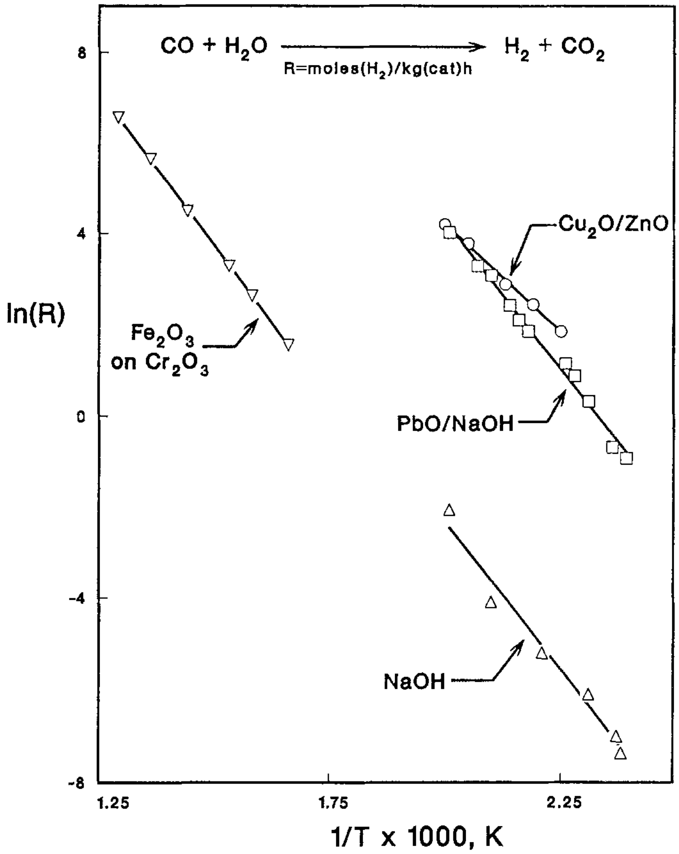

Fig. 3. Temperature dependence of the steady state rate of hydrogen production measured in a single pass tube reactor operated at one atmosphere pressure with carbon monoxide at 112 mmoles hr^{-1} and water at 44 mmoles hr^{-1} dispersed up through a triethylene glycol solution phase, 200 ml, of 0.1 M sodium formate, △, and 0.01 M lead (II) oxide in 0.1 M sodium formate, □. Comparable conditions were used for the heterogeneous iron oxide data [9] ▽, and the copper/zinc oxide system [10a] ○.

$Bu_4N^+ > Cs^+ > Na^+ > Li^+ > H^+ > Ca^{2+}$. This reactivity ordering suggests that the active formate species is the solvated anion and, most significantly, that a metal center is not required to stabilize the reaction intermediate(s) for the hydrogen activation process of (1). Furthermore, this hydroxide ion catalyzed reaction is not an unusually high energy mechanistic pathway when it is compared to either an industrially used high temperature iron oxide [9], or, alternatively, a low temperature copper/zinc oxide [10] water-gas shift catalyst, as demonstrated in fig. 3. Significantly, all of the metal oxide systems exhibit remarkably similar activation energies, 26 ± 1 kcal, for the homogeneous sodium hydroxide vs. 27 ± 0.2 kcal for the heterogeneous iron oxide, and 19 ± 0.6 kcal for the copper/zinc oxide system. Of further note, with respect to these activation parameters, is the result of experiments to selectively introduce metal ions into the homogeneous sodium hydroxide system. Thus, lead (II) oxide is soluble in this medium and shifts the sodium hydroxide system up into the general reactivity region of the copper/zinc oxide catalyst by significantly improving the net entropy of activation, intercept, while having very little effect on the activation energy, 26 ± 1 kcal, or slope.

5. Conclusions

The water-gas shift reaction is catalyzed by solvated hydroxide ion in the complete absence of a metal center by a low activation energy, 26 ± 1 kcal, mechanistic pathway. Therefore, the nucleophilic Lewis base sites situated on the hydroxide ion are an important center of reactivity and may contribute significantly to the overall activity of other metal oxide catalysts.

Acknowledgments

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References

[1] (a) R.J. Kokes, Acc. Chem. Res. 6 (1973) 226–233.
(b) H. Knozinger and S. Ratnasamy, Catal. Rev.-Sci. Eng. 17 (1978) 31–70.
(c) A.B. Anderson and J.A. Nichols, J. Am. Chem. Soc. 108 (1986) 4742–4746.
(d) J. Halpern, Annu. Rev. Phys. Chem. 16 (1965) 103.
[2] R.J. Klingler, T.R. Krause and J.W. Rathke, J. Organomet. Chem. 352 (1988) 81–94.
[3] (a) K. Wirtz and K.F. Bonhoeffer, Z. Physik. Chem. 177A (1936) 1.
(b) Y.M. Claeys, J.C. Dayton and W.K. Wilmarth, J. Chem. Phys. 18 (1950) 759.
(c) W.K. Wilmarth, J.C. Dayton and J.M. Fluornoy, J. Am. Chem. Soc. 75 (1953) 4549–4553.
(d) W.K. Wilmarth and J.C. Dayton, J. Am. Chem. Soc. 75 (1953) 4553–4556.
(e) S.L. Miller and D. Rittenberg, J. Am. Chem. Soc. 80 (1958) 64–65.
(f) J.M. Fluornoy and W.K. Wilmarth, J. Am. Chem. Soc. 83 (1961) 2257.
(g).Y. Pocker, Chem. Ind. (London) (1959) 1383.
[4] (a) C. Walling and L. Bollyky, J. Am. Chem. Soc. 83 (1961) 2968–2969.
(b) C. Walling and L. Bollyky, J. Am. Chem. Soc. 86 (1964) 3750–3752.
[5] (a) P.C. Ford and A. Rokicki, Adv. Organomet. Chem. 28 (1988) 139–217.
(b) A. Delazarche, J.P. Hindermann, R. Kieffer and A. Kiannemann, Rev. Chem. Interm. 6 (1985) 255–274.
(c) M. Iwata, Chem. Abstr. 70 (1969) 76989.
[6] R.G. Pearson and H. Mauermann, J. Am. Chem. Soc. 104 (1982) 500–504.

[7] (a) J.C. Kleingeld and N.M.M. Nibbering, J. Mass Spectrom. Ion Phys. 49 (1983) 311–318.
(b) J.C. Kleingeld, S. Ingermann, J.E. Jalonen and N.M.M. Nibbering, J. Am. Chem. Soc. 105 (1983) 2474–2475.
(c) J.F. Paulson, M.J. Henchman, Bull. Am. Phys. Soc. 27 (1982) 108.
[8] (a) D. Cremer and E. Kraka, J. Phys. Chem. 90 (1986) 33–40.
(b) G. Chalasinski, R.A. Kendall and J. Simons, J. Chem. Phys. 87 (1987) 2965–2975.
(c) J.J. Grabowski, C.H. De Puy, and V.M. Bierbaum, J. Am. Chem. Soc. 105 (1983) 2565–2571.
[9] H. Bohlbro, Acta Chem. Scand. 15 (1961) 502–520.
[10] (a) T. Van Herwÿnen and W.A. DeJong, J. Catal. 63 (1980) 83–93.
(b) D.S. Newsome, Catal. Rev.-Sci. Eng. 21 (1980) 275–318.