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ON THE MECHANISM OF THE CHROMIUM CARBONYL PHOTOCATALYZED WATERGAS SHIFT REACTION *

HERBERT NAGORSKI,
Chemische Fabrik Stockhausen GmbH, Bäkerpfad 25, D-4150 Krefeld (F.R.G.)

MANFRED J. MIRBACH,
University of Petroleum & Minerals, Department of Chemistry, Dhahran 31261 (Saudi Arabia)

and MARLIS F. MIRBACH*
Gmelin-Institut der Max-Planck-Gesellschaft, Varrentrappstr. 40-42, D-6000 Frankfurt 90 (F.R.G.)

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Summary

The chromium hexacarbonyl catalyzed watergas shift reaction is accelerated by UV irradiation and inhibited by increased CO pressure. An activation energy of 30 kJ mol^{-1} has been determined for the photochemical and one of 145 kJ mol^{-1} for the thermal reaction. Light accelerates the conversion of $Cr(CO)_6$ into $[Cr(CO)_5formate]^-$, which is thermally activated, as evidenced by in situ IR and UV spectroscopy.

Introduction

In recent years considerable effort has been directed towards elucidation of the mechanism of the homogeneously catalyzed watergas shift (WGS) reaction [1–5]. With chromium hexacarbonyl as the catalyst two mechanisms, one dissociative [1,5] (eqs. 1 and 2) and the other associative [3] (eq. 3), have been proposed. The main difference between these two proposals lies in the mode of activation of the $Cr(CO)_6$, the subsequent steps being similar in both mechanistic schemes (eqs. 4–6).

$$Cr(CO)_6 \rightleftharpoons Cr(CO)_5 + CO \tag{1}$$

$$Cr(CO)_5 + HCOO^- \rightarrow [Cr(CO)_5O_2CH]^- \tag{2}$$

$$Cr(CO)_6 + OH^- \rightarrow [Cr(CO)_5COOH]^- \tag{3}$$

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$$[Cr(CO)_5O_2CH]^- \text{ or } [Cr(CO)_5COOH]^- \rightarrow HCr(CO)_5^- + CO_2 \quad (4)$$

$$HCr(CO)_5^- + H_2O \rightarrow H_2Cr(CO)_5 + OH^- \quad (5)$$

$$H_2Cr(CO)_5 \rightarrow H_2 + Cr(CO)_5 \quad (6)$$

To gain further insight into the mechanism we have studied the chromium carbonyl catalyzed WGS reaction using high pressure photochemistry and in situ IR and UV spectroscopy.

Results and discussion

Under thermal conditions the WGS reaction results in significant conversions only at temperatures above 120°C, but it takes place under mild conditions when a solution containing KOH is irradiated with UV light (< 360 nm). Figure 1 shows the rate of the hydrogen production, expressed as turnover numbers, as a function of temperature. Although the conversion is clearly enhanced by irradiation a certain amount of thermal energy is required. Arrhenius plots of the experimental data yield activation energies of 30 kJ mol^{-1} for the photochemical and 145 kJ mol^{-1} for the thermal reaction. This shows that the rate-determining steps of the two reactions must be different.

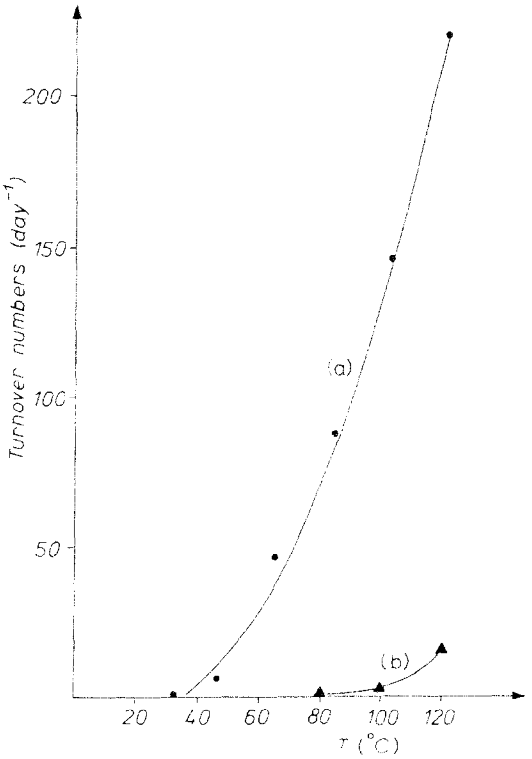


Fig. 1. Photochemical (a) and thermal (b) hydrogen production as a function of temperature. The rate of formation of H_2 is expressed as (mol H_2)×(mol $Cr(CO)_6$)$^{-1}$×(day)$^{-1}$. Activation energies: (a) E_A 30 kJ mol^{-1}, (b) $E_A = 145$ kJ mol^{-1}. Reaction conditions: 0.5 mM $Cr(CO)_6$, 0.2 M KOH in 20 ml methanol/water = 9/1; 1000 W Xe-Hg lamp, quartz filter; P(CO) 6 bar, t 18 h.

TABLE 1

FORMATION OF H_2 AND $HCOO^-$ AS A FUNCTION OF TIME [a]

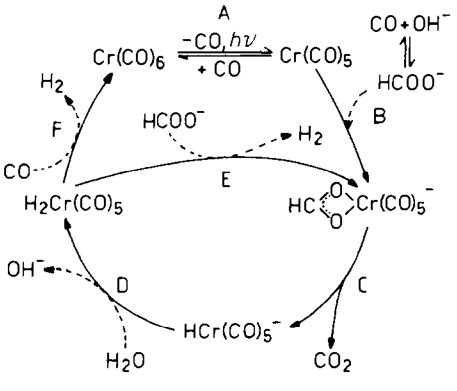
t (h)	H_2 yield ($\times 10^{-4}$ mol)	$[HCOO^-]$ (mol l^{-1})
0	0	0
3	1.1	0.15
7	2.7	0.16
9	3.3	0.16
12	4.6	0.14
15	5.5	0.15
18	6.7	0.15
24	8.7	0.16

[a] Reaction conditions: 0.5 m*M* $Cr(CO)_6$, 0.2 *M* KOH in 20 ml methanol/water = 9/1; 1000 W Xe-Hg lamp, quartz filter; *P*(CO) 6 bar, *T* 100°C.

Under irradiation the yield of hydrogen increases linearly with time, but the hydrogen formation stops when the lamp is turned off. No H_2 is formed in the subsequent dark period. Under the conditions used the formation of the formate anion from CO and OH^- is fast compared to H_2 production (Table 1).

The IR and UV spectra were measured under the conditions of the WGS reaction (Figs. 2 and 3). At low temperatures (35°C) a monosubstituted chromium carbonyl complex is formed, which has absorption bands at 1934 and 1880 cm^{-1} in the IR and at 430 nm in the UV spectrum; by comparison with authentic samples these bands are assigned to the formate complex $[Cr(CO)_5O_2CH]^-$. The bands due to the formate complex decreases with increasing temperature and the band from the unsubstituted $Cr(CO)_6$ increases, until the latter is the only detectable species at 80°C and above. Similar behaviour is observed when the CO pressure is raised from 10 to 100 bar.

Under common WGS conditions ($P(CO) > 10$ bar, $T > 80°C$), $Cr(CO)_6$ is the only light-absorbing species (> 99%). We thus conclude that the catalytic cycle is started by light induced dissociation of CO from $Cr(CO)_6$, followed by addition of formate, the latter being formed in a fast pre-equilibrium from CO and OH^-



SCHEME 1. Mechanism of the chromium carbonyl catalyzed watergas shift reaction.

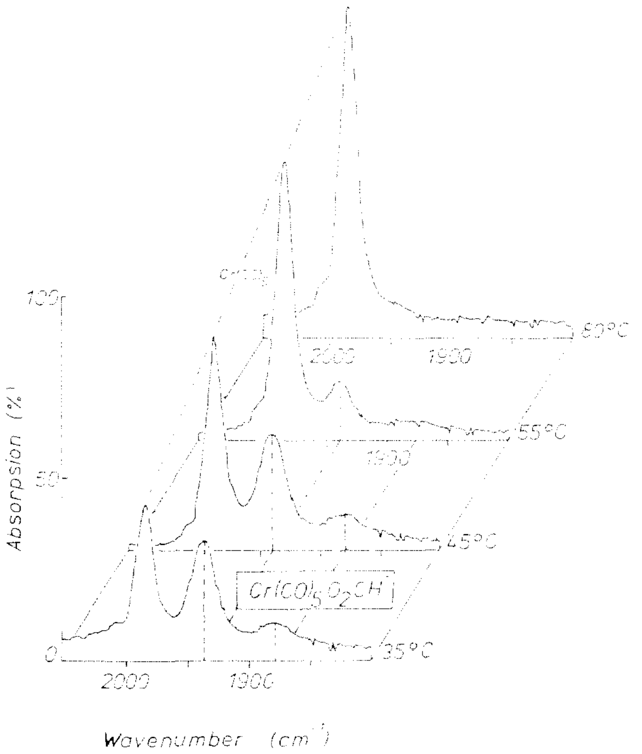


Fig. 2. Variation with temperature of the IR spectrum of a basic Cr(CO)$_6$ solution after 1 h irradiation. Reaction conditions: 4.5 mM Cr(CO)$_6$, 0.2 M KOH in 700 ml methanol/water = 9:1; 600 W medium pressure Hg lamp, Pyrex filter; P(CO) = 10 bar.

(Scheme 1). The photosubstitution is reversible, and so high CO pressure decreases the concentration of the formate complex and reduces the rate of H$_2$ formation.

The [Cr(CO)$_5$O$_2$CH]$^-$ complex is the first detectable intermediate in the catalytic

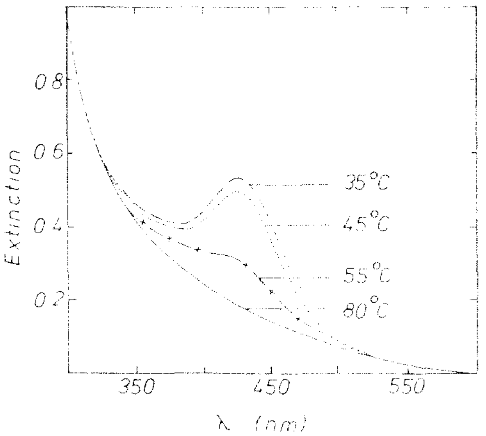


Fig. 3. Variation with temperature of the UV spectrum of a basic Cr(CO)$_6$ solution after 1 h irradiation. Reaction conditions as in Fig. 2.

cycle. Its further transformation requires thermal activation, as is evident from Fig. 2, and probably gives $HCr(CO)_5^-$ (step C in Scheme 1) and $H_2Cr(CO)_5$ (step D in Scheme 1), as proposed earlier [1,3], but these species cannot be detected by the techniques we used. The alternative possibility, that the formation of $Cr(CO)_6$ from $Cr(CO)_5O_2CH^-$ occurs via a thermally reversed photosubstitution, can be ruled out, since this would lead to reduced H_2 formation with increasing temperature, which is not observed.

In the last step of the catalytic cycle $H_2Cr(CO)_5$ can react in two ways: the H_2 can be displaced by CO, to give $Cr(CO)_6$ (step F in Scheme 1), or by the formate anion, to give the $[Cr(CO)_5O_2CH]^-$ (step E in Scheme 1). The first process dominates at the elevated CO pressures, which were used in this study and which are usual for the WGS reaction. In the absence of free CO the H_2 is displaced by a formate anion; this leads directly to a new catalytic cycle without the absorption of a new photon; such behaviour was observed in King's study of the photocatalytic formate decomposition [2]. The thermal WGS reaction requires temperatures of ca. 180°C in the absence of UV radiation, such a high temperature being necessary to induce the thermal substitution of $Cr(CO)_6$. The observed activation energy of 145 kcal mol^{-1} is in the range usually observed for thermal CO dissociation from $Cr(CO)_6$ [9], and supports the assumption of a thermal substitution of $Cr(CO)_6$ as the rate-determining step in the thermal WGS reaction.

An associative activation of $Cr(CO)_6$ by OH^- [3] should not be influenced by light and is therefore not consistent with the observed activation energies. If the associative mechanism exists at all, it must be in a minor pathway, and limited to special conditions, such as low temperatures and high CO pressure.

In conclusion, our experiments support the idea that the chromium carbonyl catalyzed water gas shift reaction has a dissociative mechanism, in which substitution of $Cr(CO)_6$ by formate is rate-determining. When this step is induced by light, it is evident that the conversion of the formate complex has the second highest activation energy. All other reactions in the catalytic cycle are fast compared to these two processes.

Experimental

A 100 ml autoclave with a quartz window was used for preparative experiments [6,7]. An external 1000 W Xe-Hg high pressure lamp was used for irradiation. The spectroscopic studies were carried out in a high pressure circulating system, consisting of a UV autoclave and high pressure IR and UV cells, as described previously [8]. In a typical experiment, the reaction mixture consisting of $Cr(CO)_6$, KOH, H_2O, and methanol was placed in the autoclave. After being flushed three times with 30 bar CO the autoclave was charged to the appropriate pressure of CO and heated to the required temperature. In preparative runs the gas phase was analyzed after 18 h by GLC. In spectroscopic studies the solution was continuously pumped through the high pressure cells and spectra were recorded at intervals.

Zeiss IMR 25 and Perkin-Elmer 283 B IR spectrometers and a Varian Cary 118 UV spectrometer were used. The gas phase was analyzed with a Fisher 1200 Gas Partitioner GC with a two column system: 1. Column 6.5′ × 1/8″ with 80–100 mesh Columnpak PQ; 2. column 11′ × 3/16″ with molecular sieve 13x; bridge current 125 mA, vaporizer at 115°C and column at 50°C, 2.5 bar N_2 ($\hat{=}$ 28 ml/min) as carrier gas.

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