Inorganica Chimica Acta, *130* (1987) 49–53

The Carbonylation of $RuCl_3 \cdot 3H_2O$ in Ethanol: an Infrared Spectroscopic Study*

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(Received November 4, 1986)

Abstract

The carbonylation of a $RuCl_3 \cdot 3H_2O$ solution in refluxing ethanol was monitored by means of infrared spectroscopy. The spectroscopic characteristics of the various intermediates were identified. Various concentrations of $RuCl_3 \cdot 3H_2O$ and various rates of CO bubbling were used to determine the dependence of the intermediates upon these parameters. Three main species were postulated to be present in solution during the carbonylation reaction.

Introduction

When carbon monoxide is bubbled through a refluxing solution of $RuCl_3 \cdot 3H_2O$ in absolute ethanol, a deep wine-red solution is obtained [1, 2]. This 'red solution' has been used since its discovery by Chatt [1] as an entry to Ru(II) and Ru(III) chemistry. A large variety of ruthenium complexes have been synthesized via the 'red solution' in the presence of various ligands. When 2-methoxyethanol is used as the solvent instead of ethanol, bubbling of carbon monoxide through the solution results in a bright lemon-yellow solution [1, 3]. The yellow solution, as well, has been used as a precursor for the preparation of a variety of ruthenium complexes [4].

However, during the course of our work with ruthenium complexes, we observed that the 'yellow solution' could also be obtained with absolute ethanol, if carbon monoxide was continuously bubbled through an already-made 'red solution'.

In this present work, we attempt to show the relationship between the 'red solution' and the 'yellow solution' as function of concentration, time and rate of CO bubbling, as well as the possible composition of these solutions.

Results and Discussion

When CO is bubbled through a refluxing solution of $RuCl_3 \cdot 3H_2O$ in absolute ethanol, and the reaction is carefully monitored by infrared spectroscopy, the spectra shown in Fig. 1 are obtained.

After 1 h, the infrared spectrum shows peaks at 1951(m), 1974(sh), 1993(w), 2045(m) and 2068(sh) cm^{-1}. With continuous CO bubbling, the infrared spectra show the following trend: the 1193 and 2068 cm^{-1} peaks increase and become the main bands in the spectrum, while the 2045 and 1951 cm^{-1} peaks decrease considerably. After 4.5 h, when the solution becomes wine-red, the 1974 cm^{-1} shoulder has completely disappeared, and the 2045 cm^{-1} band has become a shoulder. The 1951 cm^{-1} band is still present in the spectrum, even though its intensity is very low. Apparently, the 1974 and 2045 cm^{-1} bands belong to a CO-containing intermediate which is primarily formed during the early stage of the carbonylation reaction of $RuCl_3 \cdot 3H_2O$.

When CO is bubbled through the 'red solution', several changes in the spectrum occur: the 2045 cm^{-1} shoulder disappears, the 1951 cm^{-1} further decreases and a new band appears at 2131 cm^{-1}. After 16 h, when the solution turns lemon-yellow, no further changes in the spectrum are observed, and the main bands present at 1951(sh), 1993(s), 2068(s) and 2131(m) cm^{-1}.

From the above data, we note that the complete disappearance of the 2045 cm^{-1} band indicates that the reaction leading to the formation of the 'red solution' has reached completion, while the appearance of the 2131 cm^{-1} band indicates the transformation of the 'red solution' into the 'yellow solution'. The decrease of the first band and the increase of the latter have been carefully studied as a function of various reaction conditions, *i.e.* different concentrations of the starting ruthenium salt and different bubbling rates of CO. Figure 2 shows the behavior of the 2045 and 2131 cm^{-1} bands at two different initial concentrations of the ruthenium salt, and Fig. 3 shows the behavior of

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*This work was performed in part in the Department of Materials Research, The Weizmann Institute of Science, Rehovot 76100, Israel.

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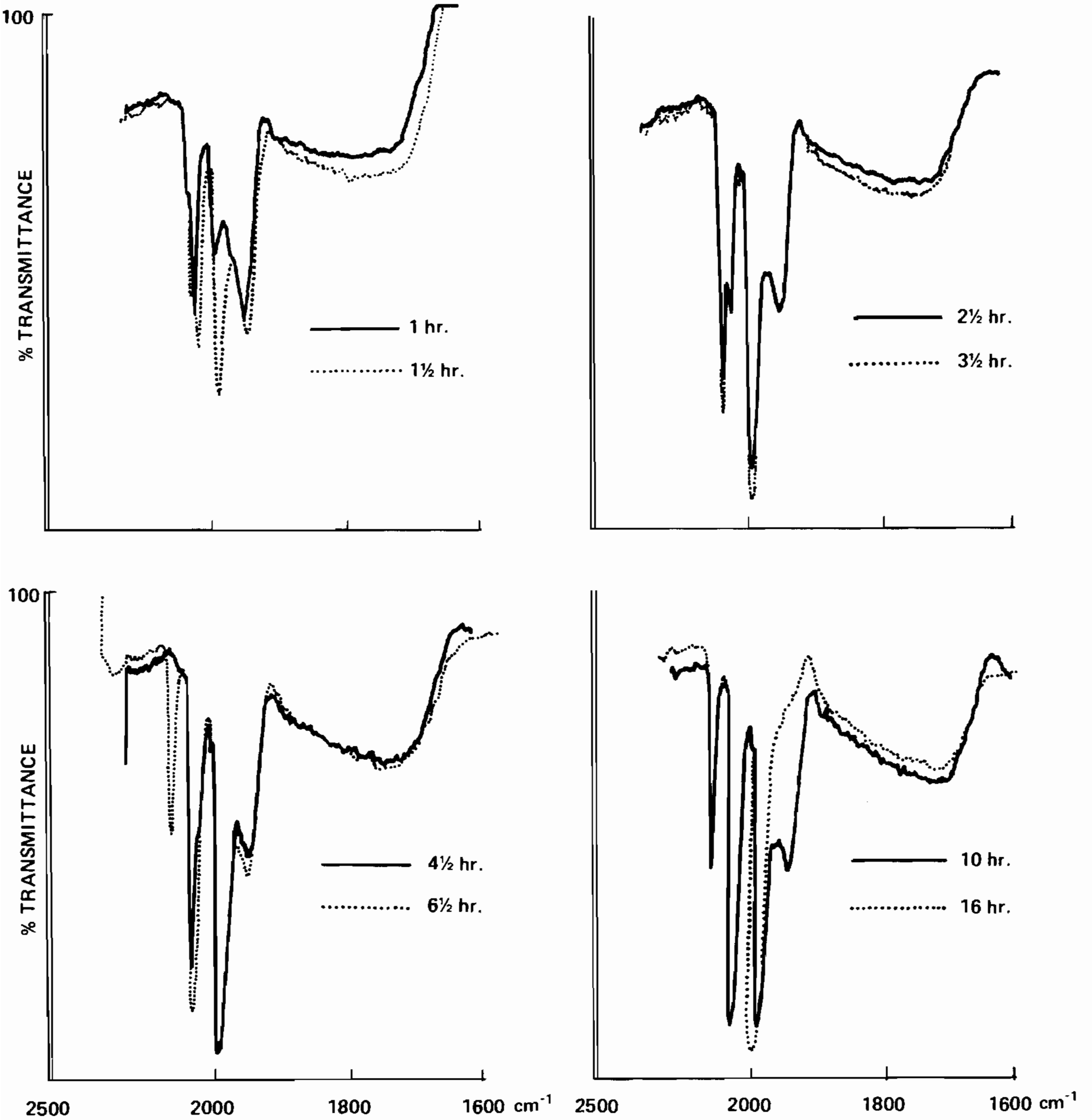

Fig. 1. Formation of the 'red' and 'yellow' solutions followed by infrared spectroscopy. The initial concentration of $RuCl_3 \cdot 3H_2O$ was 1 30 mg/ml, and the rate of CO bubbling was 12 ml/min.

these bands at two different bubbling rates of carbon monoxide.

The decrease in the initial concentration of $RuCl_3 \cdot 3H_2O$ results in the acceleration of the formation of both the 'red' and 'yellow' solutions, but the overall reaction indicates that the lifetime of the 'red solution' becomes shorter while the formation of the 'yellow solution' is predominant. On the other hand, the decrease in the rate of bubbling of CO through the solution results in a slower formation of both the 'red' and 'yellow' solutions. We should point out though, that the lower the rate of bubbling of CO, the longer the lifetime of the 'red solution'. These observations are summarized in quantitative terms in Table I. When CO bubbling through an already formed 'red solution' is completely stopped, there is no formation of the 'yellow solution', and the 'red solution' remains stable, *i.e.* exhibits the same infrared spectrum, for over 48 h under a CO atmosphere (without bubbling) and 24 h under an Ar atmosphere.

TABLE I. The Rate of Formation of the 'Red' and 'Yellow' Solutions at Various Carbonylation Conditions

Concentration (mg/ml)	Rate of CO bubbling (ml/min)	k_{obs} of formation of 'red solution' (s^{-1})	k_{obs} of formation of 'yellow solution' (s^{-1})	Lifetime of 'red solution' (min)
1/30	4	4.34×10^{-6}	7.12×10^{-6}	398
1/30	12	2.81×10^{-5}	5.71×10^{-5}	285
1/90	4	2.78×10^{-5}	5.32×10^{-5}	276
1/90	12	1.32×10^{-4}	1.82×10^{-4}	165

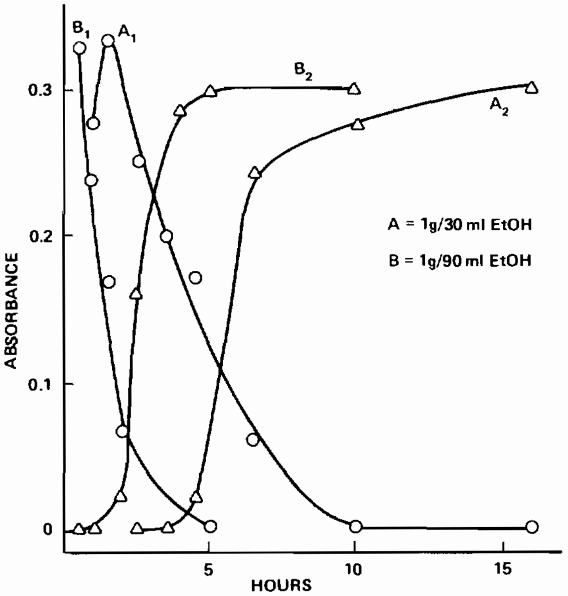

Fig. 2. Rate of formation of the 'red' and 'yellow' solutions as a function of $RuCl_3 \cdot 3H_2O$ concentrations. Rate of CO bubbling was 12 ml/min. ○, decrease of the 2045 cm^{-1} band; △, increase of the 2131 cm^{-1} band.

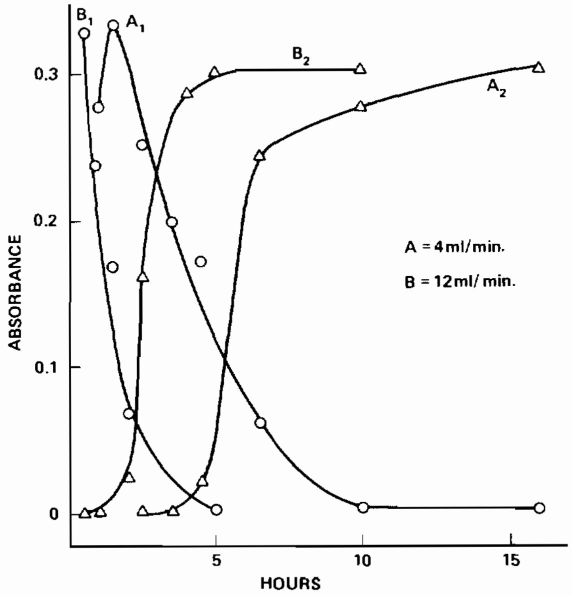

Fig. 3. Rate of formation of the 'red' and 'yellow' solutions as a function of the rate of bubbling of CO. Initial concentration of $RuCl_3 \cdot 3H_2O$ was 1/90 mg/ml. ○, decrease of the 2045 cm^{-1} band; △, increase of the 2131 cm^{-1} band.

The data presented above may suggest that not only one, but several species containing Ru, CO and Cl are present in solution as has been previously suggested by other researchers [5]. We wish to distiguish between three species: the first is basically an unstable intermediate which forms immediately upon bubbling of CO and whose CO/Ru ratio is lower than that of the other species. The other two species which form later in the reaction together with the disappearance of the first intermediate have most probably a CO/Ru ratio $\geqslant 2$. One of these complexes is mainly present in the 'red solution' and therefore it may be concluded that it is probably poorer in CO than the complex which is mainly present in the 'yellow solution'.

A good indication with respect to the nature of the compounds in solution came from another source: when $[RuCl_2(CO)_3]_2$ is synthesized from $Ru_3(CO)_{12}$ by the standard method [6], several drops of ethanol are added to help accelerate the reaction as shown below:

$$Ru_3(CO)_{12} \xrightarrow[\substack{110^\circ C \\ 5\,atm.N_2 \\ \sim 3\,ml\,EtOH}]{CHCl_3} [RuCl_2(CO)_3]_2$$

But when a larger amount of ethanol was added to the reaction mixture (~30 ml), no precipitate was obtained at the end of the reaction, only a lemon-yellow solution. This solution was analysed by infrared spectroscopy, and it exhibited the same spectrum as for the 'yellow solution'. The solution was then concentrated, hexane was added, and white crystals of $[RuCl_2(CO)_3]_2$ precipitated out. When these crystals were analyzed, they were identical to those obtained by the conventional synthesis of the Ru dimer. Freshly prepared crystals of $[RuCl_2(CO)_3]_2$ were dissolved in 1,2-dichloroethane and in ethanol,

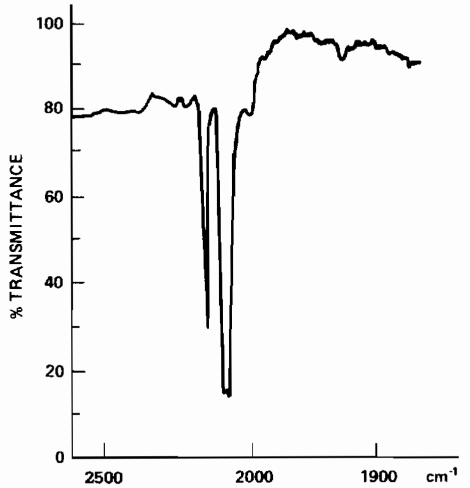

Fig. 4. Infrared spectrum of $[RuCl_2(CO)_3]_2$ in 1,2-dichloroethane (0.01 cm CaF_2 liquid cells).

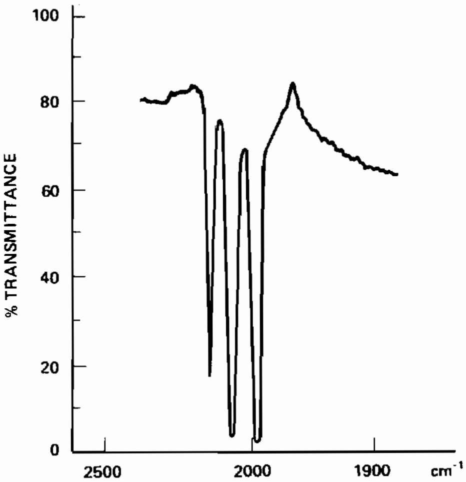

Fig. 5. Infrared spectrum of $[RuCl_2(CO)_3]_2$ in ethanol (0.01 cm CaF_2 liquid cells).

and the infrared spectra of both solutions were measured. The spectra were quite different: the one in 1,2-dichloroethane shown in Fig. 4, resembled the reported spectrum of $[RuCl_2(CO)_2]_2$ in CCl_4 [6], while the one in ethanol, shown in Fig. 5, was identical to the 'yellow solution' (compare with Fig. 1, 16 h). Since ethanol acts as a Lewis base, we can expect that in its presence, the Ru(II) dimer would dissociate (as is the case in the presence of THF [7]), and would be present in solution as the $RuCl_2(CO)_3$ monomer. Since both this and the 'yellow solution' exhibit the same spectra, we may conclude that the 'yellow solution' is mainly composed of species of the type: $RuCl_2(CO)_3$.

In the light of this evidence, we suggest the following mechanism for the carbonylation of $RuCl_3 \cdot 3H_2O$:

$$RuCl_3 \cdot 3H_2O + CO \xrightarrow[\substack{\text{reflux}\\ \sim 1\,\text{h}}]{\text{EtOH}} [RuCl_3(CO)]$$

$$[RuCl_3(CO)] + CO \xrightarrow[\substack{\text{reflux}\\ \sim 3\,\text{h}}]{\text{EtOH}} \underset{\text{red solution}}{[RuCl_2(CO)_2]}$$

$$[RuCl_2(CO)_2] + CO \xrightarrow[\substack{\text{reflux}\\ \sim 10\,\text{h}}]{\text{EtOH}} \underset{\text{yellow solution}}{[RuCl_2(CO)_3]}$$

This stepwise carbonylation mechanism may explain the kinetic features that we have observed. (a) Decrease in the initial concentration of $RuCl_3 \cdot 3H_2O$ leads to an increase in the rate of formation of both the red and yellow solutions. Moreover, the overall lifetime of the 'red solution' is shorter and the predominant product is the 'yellow solution'. (b) Decrease in the rate of bubbling of CO has an opposite effect on the reaction rates, *i.e.* decrease in the rate of formation of both solutions with a longer lifetime observed for the 'red solution'. (c) No transformation of the 'red solution' into the 'yellow solution' occurs in the absence of carbon monoxide.

Since ruthenium complexes usually have octahedral structure, and bearing in mind the effect of THF on $[RuCl_2(CO)_3]_2$, it is quite probable that the $RuCl_2(CO)_2$ and $RuCl_2(CO)_3$ complexes are present in the ethanol solution in their 'solvated' form, *i.e.* $RuCl_2(CO)_2(EtOH)_2$ and $RuCl_2(CO)_3(EtOH)$ respectively.

Experimental

$RuCl_3 \cdot 3H_2O$ was purchased from various sources: (a) Alfa Chemicals (Ventron Division), (b) Aldrich Chemicals. No differences between these two sources were observed in their reaction with carbon monoxide. All solvents (Fluka spectroscopic grade) were dried on molecular sieve and redistilled before use. All infrared spectra were recorded on a Perkin-Elmer 467B grating infrared spectrophotometer, with 0.01 cm CaF_2 liquid cells.

A typical experiment was carried out in the following way: 1 g of $RuCl_3 \cdot 3H_2O$ was dissolved in 30 ml EtOH (or 90 ml EtOH in the case of the experiments carried out with more dilute solutions), and placed in a 3-neck, 100 ml round bottom flask. The solution was flushed with Ar and then heated to 78 °C by means of a silicone oil bath. When reflux started, the Ar inlet was removed, a bubbler was inserted into the free neck and then connected to the carbon monoxide source. Samples, (0.5 ml each) were removed with a syringe through another neck which was equipped with a rubber stopper. The rate of CO bubbling was measured by connecting the carbon monoxide outlet placed on top of the cooling column to a gas burette filled with a dilute solution of $CuSO_4$, so that the blue color of the solution would give good readings of the volume displaced by CO. The total volume displaced was divided by the overall measuring time to obtain the bubbling rate as CO(ml)/min.

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