

OXIDATION OF THE $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ ANION IN AQUEOUS SOLUTION

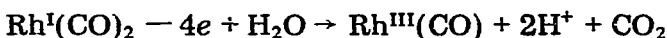
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Summary

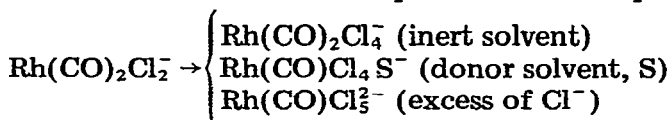
The reaction of rhodium(I) carbonyl chloride, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, with dichromate, cerium(IV) sulfate, hexachloroplatinic acid or *p*-benzoquinone in aqueous hydrochloric acid proceeds by consumption of 4 equivalents of oxidizing agent per mole of rhodium(I) in accordance with the equation



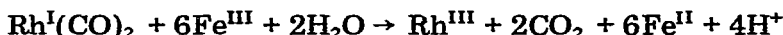
A "cyclic" oxidation mechanism is suggested.

Introduction

The action of oxidizing agents on the dicarbonyl anion $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ was reported in a number of works [1–4] published almost simultaneously in 1969. Forster [1] showed that the nature of products resulting from chlorination of salts of this anion depended on the experimental conditions:



Colton et al. [2] observed the formation of monocarbonyl anion $\text{Rh}(\text{CO})\text{Cl}_5^{2-}$ when $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ is oxidized by oxygen in aqueous hydrochloric acid. Stanko et al. [3] found that in the course of this reaction one of the carbonyl groups is oxidized quantitatively to CO_2 . James and Rempel [4] observed oxidation of both carbonyl groups of anion $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ during its interaction with excess ferric chloride. Six equivalents of oxidizing agent must be consumed per mole of dicarbonyl complex:



The above communications answer all questions concerning the nature of the oxidation products of the anion $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ under various conditions. We have obtained evidence revealing some peculiarities in the process of $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ oxidation.

Results and discussion

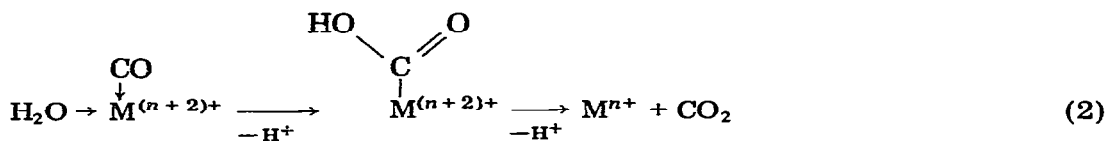
A stable light yellow solution containing rhodium as the $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ species is formed on dissolution of μ, μ' -dichlorotetracarbonyldirrhodium(I) in aqueous hydrochloric acid. Visual titration of such a solution with potassium dichromate (indicator diphenylamine) is accompanied by a consumption of 4 equivalents of oxidizing agent per mole Rh. The addition of caesium chloride to the oxidized solution precipitates a monocarbonyl rhodium(III) complex $\text{Rh}(\text{CO})\text{Cl}_3^{2-}$. The IR spectrum of the gas phase when titration has been carried out in a closed system indicates the presence of carbon dioxide and absence of carbon monoxide. The above data indicate that the oxidation of $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ may be described by eqn. 1. It should be mentioned that an oxidizing agent



should be added sufficiently slowly; otherwise there is increased consumption of the oxidizing agent and non-carbonyl complexes of rhodium(III) are formed along with $\text{Rh}(\text{CO})\text{Cl}_3^{2-}$. The reaction stoichiometry approaches that described in ref. 4.

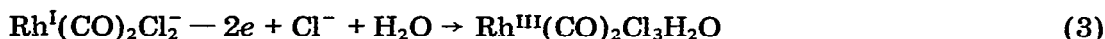
The interaction of $\text{Rh}(\text{CO})\text{Cl}_2^-$ with other oxidizing agents, hexachloroplatinic acid, cerium(IV) sulfate or *p*-benzoquinone, proceeds similarly. Rhodium(III) chloride is also capable of oxidizing $\text{Rh}(\text{CO})_2\text{Cl}_2^-$, although this reaction proceeds only to a small extent.

Taking into consideration the usual scheme of carbon monoxide oxidation by transition metal ions (eqn. 2) it would be natural to suggest that reaction 1

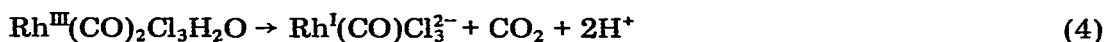


includes the following three stages:

(i) Formation of the unstable dicarbonyl rhodium(III) complex (eqn. 3).

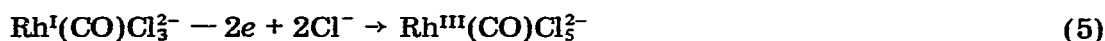


(ii) Redox interaction in its coordination sphere, according to mechanism 2 (eqn. 4). (The sum of 3 and 4 corresponds to oxidation of a carbonyl group



which requires two equivalents of oxidizing agent. Two more equivalents must be consumed for rhodium(I) oxidation).

(iii) Oxidation of the rhodium(I) monocarbonyl complex to form the end product (eqn. 5).



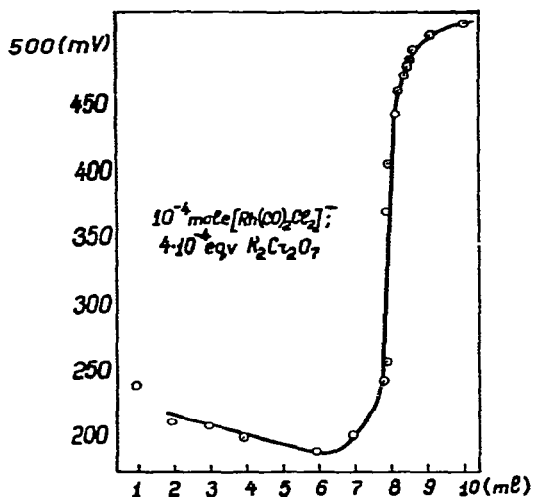


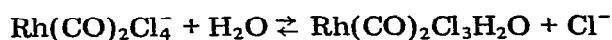
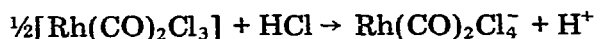
Fig. 1. Potentiometric titration of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.0194 g) in 2.5N HCl with 0.05N $\text{K}_2\text{Cr}_2\text{O}_7$.

A more detailed study showed, however, that processes that follow steps 3 and 4 are not so simple.

One jump corresponding to 4 equivalents of oxidizing agent is seen in the potentiometric titration curves of $\text{Rh}(\text{CO})_2\text{Cl}_2$ solution by dichromate, cerium(IV) and H_2PtCl_6 (Fig. 1). This means that reactions subsequent to step 3 are sufficiently rapid to prevent storage of oxidizable intermediate species (II, III etc.)

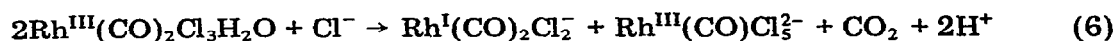
An attempt was also made to detect some carbonyl-containing intermediates by monitoring the reaction $\text{Rh}(\text{CO})_2\text{Cl}_2 + \text{PtCl}_6^{2-}$ in a non-aqueous medium (nitromethane) by IR. The measurements revealed in the solution no carbonyl species besides the initial (I) and final (IV) ones. Thus a high rate of conversion of intermediates prevented examination of some individual stages of reaction 1 by direct potentiometric or spectral measurements. One can, however, gain an insight into this reaction mechanism using data of another experiment.

Recently we have described [5] the synthesis of rhodium(III) carbonylchloride, $[\text{Rh}(\text{CO})_2\text{Cl}_3]_2$, the hydrochloric acid solution of which may be regarded as a model of the system under investigation in a state corresponding to completion of reaction 3:

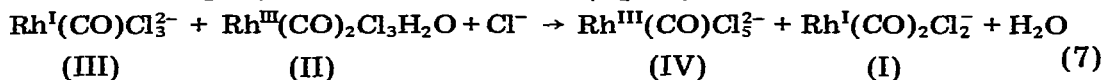


(II)

It is found that the interaction between $[\text{Rh}(\text{CO})_2\text{Cl}_3]_2$ and aqueous HCl is accompanied by CO_2 evolution and formation of $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ and $\text{Rh}(\text{CO})\text{Cl}_5^{2-}$ in equimolar amounts. The reaction is almost instantaneous. This means that dicarbonyl rhodium(III) complex II, in accordance with the above suggestion, is unstable; it suffers spontaneous redox decomposition according to eqn. 6.



In connection with reaction 6 certain speculations can be made. The distinguishing feature of reaction 6 is that only one of two participating rhodium(III) atoms undergoes reduction. The paradox is that rhodium(I) which can be formed only due to reduction of rhodium(III) by the carbonyl group is linked in product I to two carbonyl groups whereas the monocarbonyl product IV resulting from oxidation of one of the CO groups contains non-reduced rhodium(III). These peculiarities may be explained if we assume that reaction 6 consists of two stages: the dicarbonyl rhodium(III) complex undergoes initial redox decomposition according to eqn. 4 by mechanism 2 and then the resulting III interacts rapidly with the unreacted II (eqn. 7).

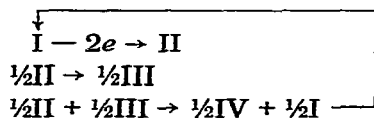


The simple reasoning that reaction 6 is a sum of reactions 4 and 7 may be formulated in a different way. The presence of the rhodium(I) dicarbonyl complex among products of reaction 6 means that rhodium(III) was reduced not at the expense of the carbonyl group bound to it but by some external reducing agent. The latter could be formed only from the initial substance; formation of this reducing agent must be accompanied by CO₂ evolution and its oxidation yields a monocarbonylrhodium(III) complex. The proposed mechanism [4 + 7 = 6] meets all these requirements.

The detailed mechanism of reaction 7 is not discussed here. It is not unlikely that it proceeds via mixed Rh^I—Rh^{III} bridged complexes as has been suggested [4].

The data from the reaction $[\text{Rh}(\text{CO})_2\text{Cl}_3]_2 + \text{HCl}_{\text{aq}}$ lead us to conclude that oxidation of the $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ anion must be described not by the sequence of eqns. 3, 4, 5 but by the sequence of 3, 4, 7. When each new portion of x_i equivalents of oxidizing agent is introduced to the solution containing originally n moles $\text{Rh}(\text{CO})_2\text{Cl}_2^-$, a new $x_i/2$ moles of the initial substance undergoes conversion according to eqns. 3, 4, 7. As a result, $x_i/4$ moles of end product IV are formed and $x_i/4$ moles of the initial I are regenerated. The amount of unreacted I after addition of a few portions of oxidizing agent is then $n - \sum x_i/4$ moles. $4n$ equivalents of oxidizing agent are required to complete the reaction ($n - \sum x_i/4 = 0$) in accordance with total stoichiometry 1.

Hence it can be suggested that a "pseudo one stage" character of reaction 1 is the consequence of its unusual "cyclic" mechanism:



Experimental

Oxidation of $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ with potassium dichromate

Upon slow (one drop per 5—7 sec) titration of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.0181 g) solution in 2.5N HCl (10 ml) with 0.1N K₂Cr₂O₇ in the presence of diphenylamine as indicator, the consumption of oxidizing agent was 3.73 ml, i.e. 4.00 equivalents per mole of rhodium. When the titration is more rapid higher consump-

tion is observed: 4.24 ml of oxidizing solution was spent on 0.0194 g $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (4.24 equivalents per mole Rh).

The following experiment was performed to identify the reaction products. $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.10 g) solution in 2.5N HCl (10 ml) was placed in a three-necked flask (argon, IR gas-cuvette, dropping-funnel with 0.1N $\text{K}_2\text{Cr}_2\text{O}_7$). The flask was filled up with argon and then was slightly evacuated (~ 200 mm Hg), and the gas-cuvette was evacuated. After gradual addition of required dichromate amounts (20.61 ml; 4 equivalents per mole Rh) the tap connecting the reaction flask and gas-cuvette was turned on and gas was forced out by the argon from the flask into the cuvette. The spectrum revealed carbon dioxide but no carbon monoxide.

The excess of CsCl was added to the oxidized solution. An orange precipitate was formed at cooling to 0° . It was filtered out, washed with small amounts of cold water, ethanol and ether. The yield was 0.14 g (50%). According to the IR spectrum [$\nu(\text{CO}) = 2118 \text{ cm}^{-1}$] and analytical data the substance was $\text{Cs}_2[\text{Rh}(\text{CO})\text{Cl}_5]$ (Found: Cl, 30.92; Rh, 18.10. $\text{Cs}_2[\text{Rh}(\text{CO})\text{Cl}_5]$ calcd.: Cl, 30.89; Rh, 17.94%). Non-quantitative precipitation of the rhodium(III) monocarbonyl complex is accounted for by the notable solubility of its caesium salt.

The addition of Bu_4NCl in excess to the filtrate induces no precipitate formation indicating the absence of unreacted rhodium(I) dicarbonyl complex in the solution.

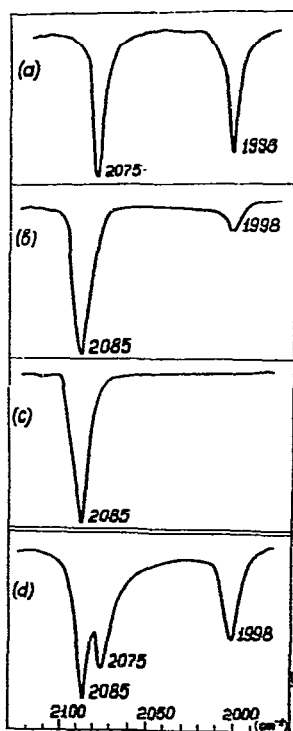


Fig. 2. IR-spectra in nitromethane: (a) $\text{Rh}(\text{CO})_2\text{Cl}_2^-$; (b) $\text{Rh}(\text{CO})_2\text{Cl}_2^- + \text{PtCl}_6^{2-}$ (Pt/Rh = 2/1) after 1 h; (c) the same after 2 h; (d) $\text{Rh}(\text{CO})_2\text{Cl}_2^- + \text{PtCl}_6^{2-}$ (Pt/Rh = 1/1).

TABLE 1

POTENTIOMETRIC TITRATION OF $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.0194 g) WITH H_2PtCl_6 (0.048N)

V(ml)	φ (mV)	V(ml)	φ (mV)	V(ml)	φ (mV)	V(ml)	φ (mV)
0.0	320	6.0	333	7.4	338	7.9	411
1.0	332	7.0	325	7.5	343	8.0	416
3.0	315	7.1	325	7.6	350	8.1	420
4.0	315	7.2	327	7.7	382	8.2	423
5.0	328	7.3	328	7.8	403	9.0	435

A jump is observed after the addition of 7.7 ml oxidizing solution, which corresponds to 4.02 equivalents per mole rhodium.

Oxidation with hexachloroplatinic acid

The reaction was carried out as described above. 0.048N H_2PtCl_6 (42.9 ml; 4 equivalents per mole Rh) was slowly added to the solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.10 g) in 2.5N HCl (10 ml). Only carbon dioxide was found in the gas-cuvette. The required amount (0.182 g) of tetrammineplatinum(II) chloride was added to the oxidized solution. The precipitate of green Magnus salt (0.282 g, 95%) was filtered out, washed and dried. As previously, $\text{Cs}_2[\text{Rh}(\text{CO})\text{Cl}_5]$ (0.143 g, $\approx 50\%$) was precipitated from the filtrate. It should be mentioned that $\nu(\text{CO})$ values in spectra of caesium salt samples obtained in various experiments somewhat differed (2104, 2112 and 2100 cm^{-1}).

Oxidation with p-benzoquinone

The reaction was performed under the same conditions. A solution of p-benzoquinone (0.12 g; 4 equivalents per 1 mole Rh) in 2.5N HCl (10 ml) was added slowly to the solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.10 g) in 2.5N HCl (4 ml). Only carbon dioxide was detected in the gas-cuvette. $\text{Cs}_2[\text{Rh}(\text{CO})\text{Cl}_5]$ (0.24 g, $\approx 80\%$) was precipitated from the oxidized solution. (The higher yield of caesium salt is accounted for by the lesser volume of the reaction mixture). The $\nu(\text{CO})$ values in spectra of caesium salt samples obtained in various experiments proved to be also different (from 2113 to 2096 cm^{-1}) but by their composition (e.g. found: Cl, 30.6; 31.9; Rh, 18.2; 18.8%) all samples are close to $\text{Cs}_2[\text{Rh}(\text{CO})\text{Cl}_5]$.

Potentiometric titration

Titration was carried out using the smooth platinum electrode; Ag/AgCl electrode was used as reference. The optimum titration regime was chosen after a few preliminary experiments. With too rapid titration the consumption of the oxidizing agent increased; when addition was too slow instability of the potential was observed due to secondary reactions.

The solutions of weighed amounts of $[\text{Rh}(\text{CO})_2\text{Cl}]$ (0.0194 g) in 2.5N HCl (20 ml) were titrated with 0.05N $\text{K}_2\text{Cr}_2\text{O}_7$, 0.048N H_2PtCl_6 , and 0.082N $\text{Ce}(\text{SO}_4)_2$. Potential values were recorded 2 min after addition of each portion of oxidizing agent. The examples are given in Table 1 and in Fig. 1.

Oxidation of $Rh(CO)_2Cl_2^-$ ions by $PtCl_6^{2-}$ ions in nitromethane

A solution of $(Bu_4N)_2PtCl_6$ (0.378 g) in nitromethane (10 ml) was added to the solution of $Bu_4N[Rh(CO)_2Cl_2]$ (0.1 g) in nitromethane (2 ml) containing an excess (0.18 g) Bu_4NCl (mole ratio $Pt^{IV}/Rh^I = 2/1$). Spectra of the solution recorded as the reaction proceeded are presented in Fig. 2a; after 1 h more than 50% of the reaction was accomplished. (The high frequency absorption maximum of the initial complex 2075 cm^{-1} is overlapped by the product band 2085 cm^{-1}). In 2 h when the reaction had been completed a yellow precipitate [a mixture of $(Bu_4N)_2[Rh(CO)Cl_5]$, $\nu(CO)$ 2073 cm^{-1} (Nujol) and $(Bu_4N)_2PtCl_4$] was isolated by ether addition. $Cs_2[Rh(CO)Cl_5]$ was precipitated by the addition of caesium chloride to an acid solution of this mixture. A similar experiment was carried out with the mole ratio Pt^{IV}/Rh^I of 1/1. The spectrum of the solution (Fig. 2d) contained in this case absorption maxima of the rhodium(I) dicarbonyl complex ($2075, 1998\text{ cm}^{-1}$) and of the rhodium(III) monocarbonyl complex (2085 cm^{-1}). Carbon dioxide was detected spectrophotometrically in the gas phase.

Interaction of $[Rh(CO)_2Cl_3]_2$ with aqueous hydrochloric acid

The reaction was carried out in a three-necked flask (argon, IR gas-cuvette, a turning vessel with aqueous HCl). $[Rh(CO)_2Cl_3]_2$ (0.42 g) was placed in the flask filled with argon. The flask and the cuvette were evacuated and while turning the vessel 2 ml 2.5N HCl was poured into the flask, whereupon the gas was displaced by argon from the reaction flask into the cuvette. The spectrum revealed CO_2 but no CO. By adding CsCl to the solution $Cs_2[Rh(CO)Cl_5]$ (0.48 g, $\approx 50\%$) was isolated. It was identified by the IR spectrum (2118 cm^{-1}) and by analysis. Upon addition of Bu_4NCl a crystalline precipitate of $Bu_4N[Rh(CO)_2Cl_2]$ identified by IR spectrum ($2054, 1974\text{ cm}^{-1}$) was separated from the filtrate. Since the latter salt does not precipitate quantitatively, an auxiliary experiment was performed, i.e. titration (potassium dichromate) of a solution obtained from the $[Rh(CO)_2Cl_3]_2 + HCl_{aq}$ reaction. 1.16 ml of 0.1N $K_2Cr_2O_7$ was spent on titration of 0.016 g $[Rh(CO)_2Cl_3]_2$ in 10 ml of 2.5N HCl, corresponding to the presence in the solution of 48% of initial rhodium as anion $Rh(CO)_2Cl_2^-$. A series of such experiments gave similar results: The amount of $Rh(CO)_2Cl_2^-$ formed made up (50 ± 2)% of the total rhodium in the solution.

Starting materials and spectra measurements

Rhodium(III) carbonyl chloride, rhodium(I) carbonyl chloride and $Bu_4N[Rh(CO)_2Cl_2]$ salt were synthesized according to procedures described previously [5, 7, 8]. Tetrabutylammonium hexachloroplatinate(IV) was prepared by neutralizing H_2PtCl_6 with Bu_4NOH in aqueous solution. IR spectra (crystalline substances as Nujol mulls) were recorded using an IKS-14A model spectrophotometer with an LiF prism.

References

- 1 D. Foster, *Inorg. Chem.*, 8 (1969) 2556.
- 2 R. Colton, R.H. Farthing and J.E. Knapp, *Aust. J. Chem.*, 22 (1969) 2011.
- 3 J.A. Stanko, G. Petrov and C.K. Thomas, *Chem. Commun.*, (1969) 1100.

- 4 B.R. James and G.L. Rempel, *J. Chem. Soc. A*, (1969) 78.
- 5 Yu. S. Varshavsky, T.G. Cherkasova and N.A. Buzina, *Zh. Neorg. Khim.*, 17 (1972) 2208; *J. Organometal. Chem.*, 56 (1973) 375.
- 6 M.J. Clear and W.P. Griffith, *J. Chem. Soc. A*, (1969) 372.
- 7 K.S. Brenner, E.O. Fischer, H.P. Fritz and C.G. Kreiter, *Chem. Ber.*, 96 (1963) 2632.
- 8 I.B. Bondarenko, N.A. Buzina, Yu. S. Varshavsky, M.I. Gelfman, V.V. Razumovsky and T.G. Cherkasova, *Zh. Neorg. Khim.*, 16 (1971) 3071.