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Stoichiometry of Sulfur Dioxide Insertion of Rhodium(I) Carbonyl Complexes by the Method of Continuous Variation

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Most of the research on insertion reactions involving transition metal complexes with sulfur dioxide in the last decade has been centered on synthesis, characterization, and molecular structure [1–6].

For the reaction between $[Rh(CO)_2Cl_2]^-$ and SO_2 the molar ratio of the metal to the reagent in the complex is not known colorimetrically.

In this paper the method of continuous variation [7] has been employed to determine the molar ratio (stoichiometry) of the sulfur dioxide insertion reaction of rhodium(I) carbonyl complexes. This reaction has been followed spectrophotometrically at 500 nm at room temperature. The molar ratio of the insertion of sulfur dioxide molecule in $[Rh(CO)_2Cl_2]^-$ complex ion was found to be 1:1 initially and 2:1 after 48 hr.

Experimental

Materials

All chemicals used for the preparation of compounds and analytical procedures were of reagent quality unless otherwise specified. Rhodium trichloride was from Johnson Matthey Chemicals Ltd., London. Liquified sulfur dioxide was from BDH Chemicals Ltd., London.

The complex ion $[Rh(CO)_2Cl_2]^-$ was prepared by passing carbon monoxide through an ethanolic solution of rhodium trichloride (0.20 g in 30 ml ethanol) [8]. The solution was then refluxed for five hours at 75 °C with continuous stirring. During this time the color of the solution slowly changed from dark red to pale yellow. In this preparation ethanol acts as a reducing agent on rhodium yielding hydrogen ions in the process as the cation.

All complex solutions were prepared in absolute ethanol media. The concentration of $[Rh(CO)_2Cl_2]^-$ was 7.0×10^{-2} *M* and the concentration of SO_2 was 7.0×10^{-2} *M*.

The reaction of SO_2 in $[Rh(CO)_2Cl_2]^-$ was followed at 500 nm with a Unicam SP 8000 spectrophotometer. At this wavelength both reactants have no absorption. A series of solutions of varying composition of SO_2 and $[Rh(CO)_2Cl_2]^-$ were prepared as is shown in Table I.

TABLE I. Absorbances of Different Mixtures of $[Rh(CO)_2Cl_2]^-$ with SO_2 at 500 nm. The Concentration of $[Rh(CO)_2Cl_2]^-$ was 7.0×10^{-2} *M* and the Concentration of SO_2 was 7.5×10^{-2} *M*.

$[Rh(CO)_2Cl_2]^-$ % Composition	SO_2		A_1[a]	A_2[b]
	Vol, ml	Vol, ml		
0	0	10.0	0	0
9.3	1.0	9.0	0.06	0.08
16.0	2.0	8.0	0.10	0.17
27.5	3.0	7.0	0.17	0.24
38.5	4.0	6.0	0.22	0.32
58.5	6.0	4.0	0.26	0.53
68.5	7.0	3.0	0.18	0.52
78.5	8.0	2.0	0.13	0.33
88.5	9.0	1.0	0.07	0.18
100.0	10.0	0	0	0

[a]A_1 = Absorbance taken after 3 hr. [b]A_2 = Absorbance taken after 48 hr.

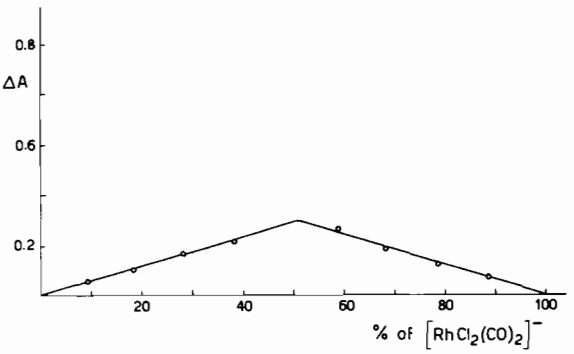

Figure 1. Plot of change in absorbance *versus* the percentage composition of $[Rh(CO)_2Cl_2]^-$ after 3 hr at temperature = 25 ± 0.1 °C.

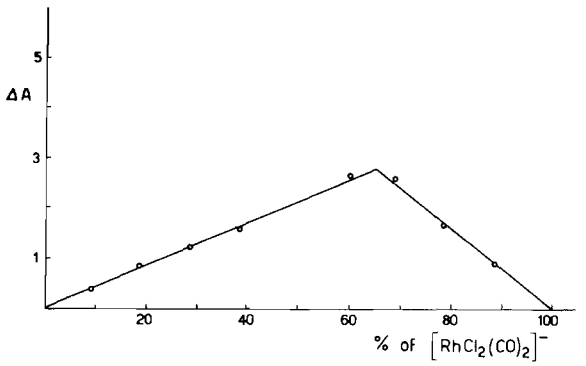

Figure 2. Plot of change in absorbance *versus* the percentage composition of $[Rh(CO)_2Cl_2]^-$ after 48 hr at temperature = 25 ± 0.1 °C.

The difference between the measured absorbance and the absorbance calculated for the mixed constituents on the assumption of no reaction between them was taken at 500 nm. The difference in absorbance was plotted against the percentage composition of $[Rh(CO)_2Cl_2]^-$ as is shown in Figs. 1 and 2.

Results and Discussion

The overall stoichiometry for the reaction between $[Rh(CO)_2Cl_2]^-$ and SO_2 after 3 hr and 48 hr was found to be as given in Eqns. (1) and (2):

$$[Rh(CO)_2Cl_2]^- + SO_2 \xrightarrow[25\ °C]{3\ hr} [Rh(SO_2)(CO)_2Cl_2]^- \quad (1)$$

$$[Rh(CO)_2Cl_2]^- + 2SO_2 \xrightarrow[25\ °C]{48\ hr} [Rh(SO_2)_2(CO)_2Cl_2]^- \quad (2)$$

Our present results yield a curve showing a maximum at the percentage corresponding to that in $[Rh(CO)_2Cl_2]^-$. The sharpness of the breaks in the curves of both Figs. 1 and 2 of the identification of the complex depends on the magnitude of the stability constant. The ratio of SO_2 to $[Rh(CO)_2Cl_2]^-$ was found to be 1:1 after three hours as is shown in Fig. 1 and 2:1 after 48 hours as is shown in Fig. 2. Each of the values used in plotting the figures resulted from four or more individual runs.

Acknowledgment

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