

BASE HYDROLYSIS REACTION OF DICHLOROETHOXYOXOBIS(TRIPHENYLPHOSPHINE) RHENIUM(V)

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Introduction

By the success in the diagnostic applications of ^{99m}Tc -labeled radiopharmaceuticals, current interest has been focused on radiopharmaceuticals for therapy. Among them rhenium isotopes (^{186}Re and ^{188}Re) have several advantages that their nuclear properties are suitable for imaging and their chemical properties are similar to those of technetium[1]. However, substitution-inert character of rhenium compounds has brought about some difficulties in the syntheses of rhenium-radiopharmaceuticals.

Systematic studies on the substitution reactions of rhenium complexes have not been made. Mechanism of the hydrolysis reaction of $[\text{Re}(\text{tu})_6]^{3+}$ has been established, in which there exists the equilibrium between $[\text{Re}(\text{tu})_6]^{3+}$ and $[\text{Re}(\text{H}_2\text{O})(\text{tu})_5]^{3+}$ and then hydrolysis of $[\text{Re}(\text{H}_2\text{O})(\text{tu})_5]^{3+}$ takes place in the presence of a large excess thiourea over rhenium[2]. The present paper will report the base hydrolysis of dichloroethoxyoxobis(triphenylphosphine)-rhenium(V) ($[\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2]$). This compound has been used for the synthesis of Re(V) and Re(IV) complexes as a starting material[3,4].

Experimental

Dichloroethoxyoxobis(triphenylphosphine)rhenium(V) was synthesized by modifying the method described in the literature[3,5]: that is, concentrated hydrochloric acid solution containing ammonium perrhenate was diluted with ethanol and the mixture was heated for 5 min. To this hot solution a hot ethanol solution of triphenylphosphine was added. Green crystals were collected by filtration. The synthesized complex was further purified by recrystallization from benzene-petroleum ether.

Kinetic runs were carried out by means of a solvent extraction method at 25 °C. Thus, an aqueous solution of sodium hydroxide was added to a chloroform solution containing $[\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2]$ to initiate the base hydrolysis reaction. Ionic strength of the aqueous solution was adjusted to 1 M with sodium chloride. Aliquots were taken from the reaction mixture at suitable intervals. The concentration of rhenium in the organic phase was determined spectrophotometrically.

Results and Discussion

When an aqueous solution of sodium hydroxide was added to a chloroform solution of $[\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2]$, in the organic phase the absorbance at 273 nm decreased with time. Finally the UV spectrum with the absorption maximum at 262 nm was obtained, corresponding with that of free triphenylphosphine. This means that by the attack of hydroxide ion the complex liberates an anion ligand and a charged complex was then extracted into the aqueous phase. In the present system, the initial concentration of $[\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2]$ ($[\text{C}]$) was much lower than that of hydroxide ion, the rate of base hydrolysis of $[\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2]$ ($-\text{d}[\text{C}]/\text{d}t$) is supposed to be a pseudo first order with respect to $[\text{C}]$. If triphenylphosphine liberated from the complex remains in the organic phase, the following equation could be derived.

$$\ln \frac{[\text{C}]_t}{[\text{C}]_0} = \ln \frac{(A_t - A_\infty)}{(A_0 - A_\infty)} = k_{\text{app}} t \quad (1)$$

where A is the absorbance at 273 nm and k_{app} is the apparent first order rate constant.

On the basis of linear plots of $\ln\{(A_t - A_\infty)/(A_0 - A_\infty)\}$ against time, the apparent rate constants k_{app} were obtained. On the basis of the dependence of the apparent rate constant on the concentration of hydroxide ion, the apparent rate constant could be expressed as

$$k_{\text{app}} = k [\text{OH}^-] \quad (2)$$

where k is the rate constant for the base hydrolysis of $[\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2]$. Thus the rate constant k was determined to be

$$k = 1.03 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1} \\ (25^\circ \text{C}, I = 1.0 \text{ M})$$

The reaction mechanism for the base hydrolysis of $[\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2]$ was compared with that of various technetium β -diketone complexes.

References

1. K. Hashimoto, K. Yoshihara, "Topics in Current Chemistry, 176, Technetium and Rhenium", (ed. by K. Yoshihara, T. Omori), Springer-Verlag, Berlin, 1996, pp. 275-291.
2. T. Omori, M. Yuasa, R. Shinoda, Y. Tanaka, M. Kawasaki, H. Suganuma, "Proceedings of the 1st Seminar on Application of Accelerator Radiation", Hsinchu, Taiwan, Dec. 26-27, 2000, p. 145.
3. N. P. Johnson, C. L. J. Lock, G. Wilkinson, *J. Chem. Soc.*, 1054 (1964).
4. D. E. Grove, N. P. Johnson, C. L. J. Lock, G. Wilkinson, *J. Chem. Soc.*, 490 (1965).
5. N. P. Johnson, C. L. J. Lock, G. Wilkinson, *Inorg. Synth.*, **9**, 145 (1967).