Substitution Reactions of Technetium Complexes

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Success of the diagnostic application of radiopharmaceuticals labeled with ^{99m}Tc suggests a possibility that these are used as therapeutic agents in nuclear medicine. Thus, much attention has been paid for the syntheses of $^{186,188}Re$-labeled radiopharmaceuticals by applying the procedures developed in the syntheses of ^{99m}Tc-labeled complexes. Taking into account these features, the present status in the substitution reactions of technetium complexes will be considered.

1. Ligand exchange reaction

In general, low spin Tc(III)[d^4] and Tc(IV)[d^3] complexes are considered to be substitution-inert. For example, no isotopic exchange reactions by ligand substitution

$$[MCl_5\ ^{36}Cl]^{2-} + Cl^- \rightleftharpoons [MCl_6]^{2-} + {}^{36}Cl^-$$
$$[MBr_5\ ^{82}Br]^{2-} + Br^- \rightleftharpoons [MBr_6]^{2-} + {}^{82}Br^- \qquad (1)$$

take place at room temperature, where M designates Tc or Re. However, the excahnge reactions proceed slowly in the 8 M solutions of their corresponding acid at 60℃. The rates, R, were found to be 8.1×10^{-7} M s^{-1} for $TcCl_6^{2-}$, 3.6×10^{-8} M s^{-1} for $ReCl_6^{2-}$, 1.4×10^{-4} M s^{-1} for $TcBr_6^{2-}$, and 2.3×10^{-6} M s^{-1} for $ReBr_6^{2-}$[1]. These results show that the exchange reactions for Tc complexes proceed faster than those for Re complexes.

The ligand exchange reaction for Tc(III) complex was found in the system of tris(acetylacetonato)technetium(III)($Tc(acac)_3$)[2]. The substitution-inert character of $Tc(acac)_3$ has already been pointed out in its nuclear synthesis by the $^{97}Ru(acac)_3$ (γ, n) reaction[3]. The ligand exchange reaction in acetylacetone solution is expressed as

$$^{99}Tc(\ ^*acac)(acac)_2 + Hacac \rightleftharpoons {}^{99}Tc(acac)_3 + H^*acac \qquad (2)$$

where H^*acac denotes Hacac[2-^{14}C]. The observed rate depends on the concentration of $Tc(acac)_3$, but is independent of the concentration of acetylacetone and water. Thus, the rate, R, can be expressed as