Inorganica Chimica Acta, 161 (1989) 151–152

Cleavage of Ligand in a Tc/Schiff Base System: An Unusual Reaction

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(Received March 2, 1989)

Tridentate Schiff-base ligands H_2L react with oxotechnetium precursors such as Tc gluconate or tetrachlorooxotechnetate(V), either alone or in the presence of coligands, in the 'normal' way forming oxotechnetium(V) complexes of the intact tridentate ligand. Thus, reaction of the Schiff-base ligand with $TcOCl_4^-$ yields the complexes TcOLCl [1]. In the presence of bidentate Schiff bases HL_1 or thiols RSH, 'mixed' ligand complexes of the formulae $TcOLL_1$ [2] and TcOL(RS) are obtained. The latter compounds have also been obtained by the joint action of Schiff bases and thiols on the less reactive Tc gluconate [3].

There is, however, a significant dependence of the nature of the compounds formed in the reaction between Schiff bases and Tc gluconate on the pH of the reaction milieu. In this paper we report on the reaction of different Schiff bases (derived from the condensation of 2-aminobenzenethiol, H_2abt, with salicylic aldehyde, diacetyl and acetylacetone) with Tc gluconate or pertechnetate/dithionite in alkaline media, and the preferred formation of $[TcO(abt)_2]^-$ under these conditions. The mechanism of this unusual reaction is discussed.

Experimental

Tc(V) gluconate was prepared as described in ref. 4; Schiff bases were obtained according to standard procedures by condensation of 2-aminobenzenethiol with (a) salicylic aldehyde, (b) acetylacetone and (c) diacetyl.

Tetrabutylammonium Bis(2-amidobenzenethiolato-(2⁻)-S, N)oxotechnetate(V), $Bu_4N[TcO(abt)_2]$

An aqueous acetonic solution (2:1 vol./vol.) of Tc(V) gluconate (50 μmol based on TcO_4^-) was adjusted to pH 11 by 1 N NaOH. The corresponding Schiff-base ligand (a)–(c) (125 μmol), dissolved in acetone, was added to this mixture. The colour turned to orange–brown immediately. Addition of 50 mg tetrabutylammonium bromide gave a brown precipitate which was filtered off, washed first with water and then with cold methanol and dried *in vacuo*; melting point 154–156 °C (methanol/ethyl acetate). Analytical data correspond to the formula $NBu_4[TcO(abt)_2]$; IR (cm^{-1}), 920 Tc=O. Yields are about 60% based on Tc gluconate.

The identity of the substances obtained by the reaction of Tc gluconate with different ligands (a)–(c) with $Bu_4N[TcO(abt)_2]$, described in ref. 5, was confirmed by TLC, melting point and identical IR, ^1H NMR and UV–Vis spectra.

Results and Discussion

Despite the fact that neutral oxotechnetium(V) complexes of Schiff-base ligands are obtained in acid or neutral aqueous solutions, the only product of the reaction of the Schiff bases of 2-aminobenzenthiol (H_2abt) in alkaline media is a red-coloured anionic compound which was separated as the tetrabutylammonium salt. This is also true both for ligand exchange reaction on tetrachlorooxotechnetate and for reduction of pertechnetate by dithionite in the presence of Schiff bases in alkaline media. The analytical data [5] correspond to $Bu_4N[TcO(abt)_2]$. According to these data, the compound is identical with that prepared earlier by Gerber *et al.* [6] and later correctly formulated on the basis of X-ray crystallography [7].

These findings suggest that the Schiff-base ligand was cleaved, delivering H_2abt for complexation of Tc, as can be seen in Fig. 1. The mechanism of this rather unexpected reaction cannot be understood *a priori*. Primary cleavage of the Schiff base is unlikely because in alkaline media the rate of hydrolysis is very low. It would appear that there is a complicated mechanism involving the Tc=O core. Assuming an attack of the thiol group to Tc as the first step, a polarizing effect caused by the Tc=O

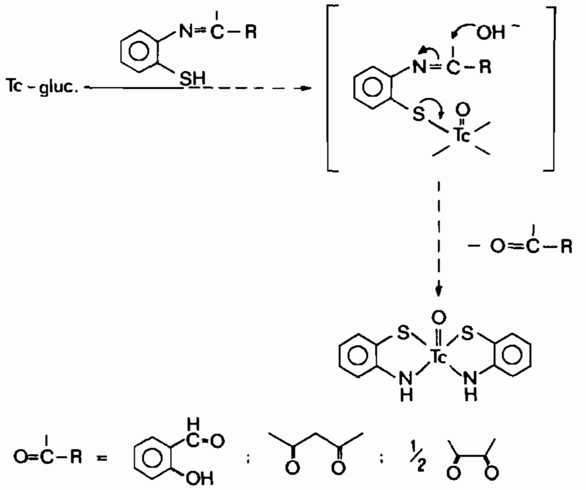

Fig. 1. Reaction of Tc gluconate with Schiff bases of H_2abt in alkaline medium.

0020-1693/89/$3.50

core may act on the imine group directly or, more likely, by a conjugation effect via the aromatic system. As a consequence, the C=N group is highly polarized and nucleophilic attack on the carbon atom of the C=N group may occur. In alkaline medium, hydrolysis leads to Tc–N bond rupture. Subsequent attack of the resulting amino group to vacant coordination sites of Tc results in fixation of the abt ligand to give $[TcO(abt)_2]^-$.

The effect of activating the ligand moiety by the Tc core is documented by:

(i) racemization of the oxotechnetium(V) complex of *meso*-2,3-dimercaptosuccinic acid dimethyl ester in alkaline medium due to the acidification of protons in the ligand skeleton [8];

(ii) the activation of an α-carbon atom towards nucleophilic replacement, resulting in the dealkylation reaction observed on neutral [TcO(ema)R] [9].

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