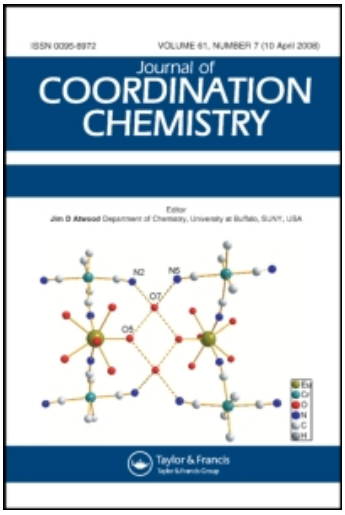

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^{31}P NMR STUDIES OF REDOX REACTIONS OF BIS (TRIALKYLPHOSPHINE) GOLD(I) BROMIDE (ALKYL = METHYL, ETHYL) WITH DISULPHIDE AND DISELENIDE LIGANDS

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Redox reactions of bis (trialkylphosphine) gold(I) bromide (alkyl = methyl, ethyl) with two diselenides (R′Se–SeR′), selenocystine and selenocystamine and their corresponding disulfides were studied in D_2O by ^{31}P NMR spectroscopy. Upon interaction of diselenides with $(Me_3P)_2AuBr$ or with $(Et_3P)_2AuBr$, the Se–Se bond is broken, resulting in the formation of R_3PAu^+, R′SeH, R′Se–Au–PR_3, R_3PO and $(AuSeR')_n$. Second-order rate constants were determined for the decomposition of $(R_3P)_2AuBr$. Selenocystamine reacts with $(Et_3P)_2AuBr$ about 100 times faster than its corresponding disulfide. However, cystamine reacts twice as fast with $(Me_3P)_2AuBr$ compared to its corresponding diselenide.

Keywords: Gold(I) thiomalate; Diselenide; Selenocystine; Selenocystamine; NMR

INTRODUCTION

Gold(I) compounds are used clinically in the alleviation of symptoms associated with rheumatoid arthritis. This is because they have a high affinity and hence selectivity for –SH and –SeH ligands. It is well known that disodium Au(I) thiomalate (AuStm "Myocrisin") is a potent inhibitor of sulphydryl–disulphide exchange reactions and can participate in facile sulphydryl ligand-exchange reactions. Gold(I) is also known to be a strong inhibitor of the catalytic activity of Se-glutathione peroxidase, the only mammalian selenoprotein with known catalytic activity [1,2].

We are interested in the chemistry of $(Et_3P)_2Au^+$ because it has been reported that orally administered $(Et_3P)_2Au^+$ has similar biological activity to auranofin (a second-generation, orally active gold drug) in the adjuvant-induced arthritic rat model. Recent reviews by McKeage *et al.* [3] and Tiekink [4] show that Et_3PAuCl and other gold(I) phosphine complexes act as potential antitumor agents.

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Reduction of disulfide bonds of human blood and bovine serum albumin with $(Et_3P)_2Au^+$ *in vitro* has been reported [5–7]. To gain further insight into the mechanism of the redox reactions, we studied the reactions of disulphides and diselenides with $(Et_3P)_2Au^+$ and $(Me_3P)_2Au^+$. There are no known diselenide bonds *in vivo*; however, the chemistry of gold(I) drugs with selenium-containing amino acids is important since selenocysteine is present at the active binding site of Se-glutathione peroxidase [1,2].

In this article, we report second-order rate constants for reactions between disulphides/diselenides and $(Et_3P)_2AuBr$ and $(Me_3P)_2AuBr$ studied by ^{31}P NMR spectroscopy.

EXPERIMENTAL

Chemicals

Me_3P, Et_3P and AuBr were obtained from the Strem Chemical Co. Selenocystine (CysSeSeCys), selenocystamine dihydrochloride (CymSeSeCym) and their analogous disulfides were obtained from the Sigma Chemical Co. D_2O was purchased from the Fluka Chemical Co. $(Et_3P)_2Au^+$ and $(Me_3P)_2Au^+$ were prepared from Et_3PAuBr and Me_3PAuBr as described in the literature [7].

^{31}P NMR Measurements

^{31}P NMR spectra were recorded on a Jeol JNM-LA 500 NMR spectrometer operating at 202.35 MHz with ^1H broadband decoupling, at 297 K, using a 0.269-s acquisition time, 60.00-s pulse delay and 6.20-μs pulse width (45°). The ^{31}P NMR chemical shifts were measured relative to TMP as internal reference.

pH Measurements

All pH measurements were made at 24°C with a Fischer Accumet pH meter (model 630). The term pH* indicates the actual meter reading for D_2O solutions with no correction for deuterium isotope effects. The pH was adjusted using DCl and NaOD.

RESULTS

Reaction Between $(Et_3P)_2Au^+$ and Senocystamine (CymSeSeCym): Reaction A

$(Et_3P)_2AuBr$ and CymSeSeCym were dissolved in D_2O at pH* 7.4. First, $(Et_3P)_2AuBr$ was dissolved in a minimum amount of CD_3OD (1 to 2 drops) and the the required amount of D_2O was added. Figure 1(a) shows the ^{31}P NMR spectrum of $(Et_3P)_2AuBr$: CymSeSeCym at a 1 : 1 ratio (0.01 M). The resulting solution was clear. As soon as these two solutions were mixed, the ^{31}P NMR showed four resonances at 44.0, 34.6, 61.7 and 58.5 ppm. The resonance at 44.0 ppm is due to $(Et_3P)_2Au^+$ [7]. The resonance at 34.6 is due to Et_3PAu^+, and that at 61.7 ppm is due to Et_3PO (Table I). The resonance at 58.5 ppm will be identified later. After 8 h reaction, the

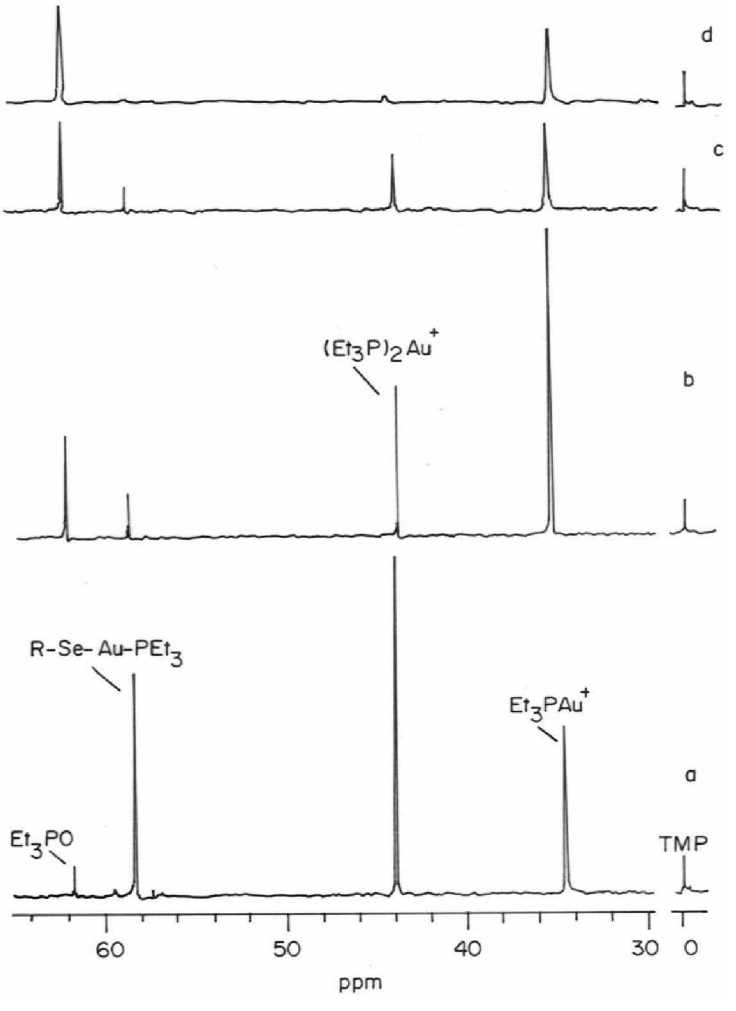

FIGURE 1 202.35 MHz $^{31}P\{^1H\}$ spectra of 0.01 M $(Et_3P)_2Au^+$: 0.01 M CymSeSeCym in D_2O at various time intervals; (a) 10 min, (b) 8 h, (c) 24 h, (d) 56 h.

TABLE I ^{31}P NMR chemical shifts of various species in D_2O (with a trace of CD_3OD)

Species	*Resonance assignment* (δ in ppm)	*Ref.*
$(Et_3P)_2AuBr$	44.0	[5,7]
Et_3PAuBr	34.6	[5,7]
Et_3PO	61.7	[5,7]
CymSe–Au–PEt_3	58.5	This work
$(Me_3P)_2AuBr$	4.3	[15]
Me_3PAuBr	−3.1	[15]
CymSe–Au–PMe_3	30.9	This work
Me_3PO	50.1	[15], This work
Me_3PSe[a]	9.93	This work

[a]In CD_3OD.

^{31}P NMR was recorded and is shown in Fig. 1(b). The resonances at 44.0 and 58.5 decreased and those at 34.6 and 61.7 increased in intensity.

A probable reaction of $(Et_3P)_2Au^+$ with R–Se–Se–R is given below. In the first step, reduction of the Se–Se bond takes place via the $(Et_3P)_2Au^+$ complex as shown in Eq. (1).

$$(Et_3P)_2Au^+ + R{-}Se{-}Se{-}R + H_2O \rightarrow 2R{-}Se{-}H + Et_3PO + Et_3PAu^+ \quad (1)$$

In the second step, binding of Et_3PAu^+ with R–Se–H takes place and R–Se–Au–PEt_3 is formed, Eq. (2). The resonance at 58.5 is assigned to R–Se–Au–PEt_3, based on Eqs. (1) and (2).

$$R{-}Se{-}H + (Et_3P)_2Au^+ \rightarrow R{-}Se{-}Au{-}PEt_3 + Et_3P + H^+ \quad (2)$$

In the third step, Et_3P produced in Eq. (2) above can also reduce unreacted diselenide, Eq. (3)

$$R{-}Se{-}Se{-}R + Et_3P + H_2O \rightarrow 2R{-}Se{-}H + Et_3PO \quad (3)$$

The R–Se–H generated can further react to give R–Se–Au–PEt_3 as shown in Eq. (2). The Et_3P generated in Eq. (3) can also be oxidized to form Et_3PO, which resonates at 61.7 ppm [7].

Unreacted diselenides can also react with R–Se–Au–PEt_3 as follows:

$$R{-}Se{-}Se{-}R + R{-}Se{-}Au{-}PEt_3 + H_2O \rightarrow 2R{-}Se{-}H + Et_3PO + Au{-}Se{-}R \quad (4)$$

As the reaction proceeds (Fig. 1), Et_3PO is formed as indicated in Eqs. (1) and (3); this is indicated by the consistent increase in resonance intensity at 61.7 ppm. A decrease in intensity at 44.0 ppm shows that $(Et_3P)_2Au^+$ is consumed as indicated in Eqs. (1) and (2). The reaction sequence indicated in Eqs. (1) to (4) does not necessarily follow in the order as written, but reactions can occur simultaneously, or in any sequence.

A decrease in intensity at 58.0 ppm shows consumption of R–Se–Au–PEt_3 as in Eq. (4). Increasing intensity at 34.0 ppm shows increasing concentrations of Et_3PAu^+, as in Eq. (1). At the end of the experiment some precipitate is formed and the only resonance observed is due to Et_3PO, indicating that eventually Au–Se–R precipitates.

Reaction Between $(Et_3P)_2Au^+$ and CymSSCym

Figure 2 shows the ^{31}P NMR spectrum of $(Et_3P)_2Au^+$: CymSSCym at a 1 : 1 ratio (0.01 M), pH* 7.2 in D_2O. As soon as the solutions were mixed only one resonance appeared at 44.0 ppm, corresponding to $(Et_3P)_2Au^+$ [7]. After 15 h a ^{31}P spectrum of the same solution showed a resonance at 61.7 ppm corresponding to Et_3PO, thus showing reaction of $(Et_3P)_2Au^+$ with CymSSCym. After 36 h the ^{31}P NMR spectrum showed completion of the reaction marked by the absence of any resonance at 44.0 ppm ($(Et_3P)_2Au^+$) and the emergence of a resonance at 34.6 ppm due to Et_3PAu^+.

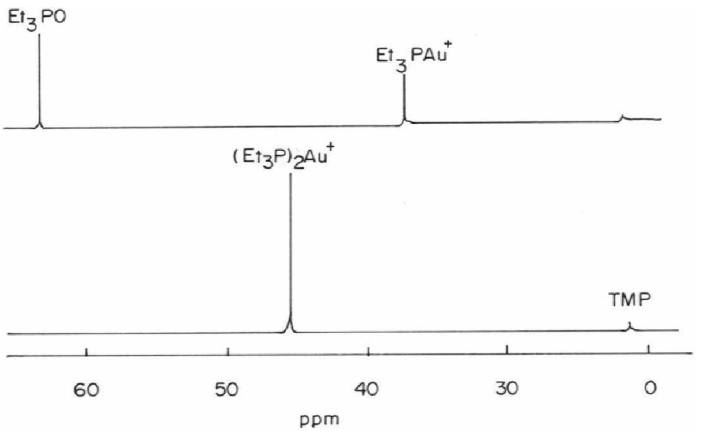

FIGURE 2 202.35 MHz $^{31}P\{^{1}H\}$ spectra of 0.01 M $(Et_3P)_2Au^+$: 0.01 M CymSSCym in D_2O after 10 min (lower) and 36 h (upper).

It should be noted that no CymS–Au–PEt_3 species was observed throughout the reaction unlike the previous experiment where CymSe–Au–PEt_3 was detected.

Reaction of $(Et_3P)_2Au^+$ and Selenocystine (CysSeSeCys)

The reaction of selenocystine (CysSeSeCys) with $(Et_3P)_2Au^+$ was carried out at pH* 12.2 in D_2O using equimolar concentrations (0.01 M) of both reagents. CysSeSeCys is not soluble at neutral pH but dissolves only in basic media. The ^{31}P NMR spectrum of the reaction mixture shows resonances at 44.0 and 34.6 ppm, indicating the presence of $(Et_3P)_2Au^+$ and Et_3PAu^+. No change in resonance intensity of either species was observed even after 48 h. CysSeSeCys is much less reactive towards $(Et_3P)_2Au^+$ than CymSeSeCym. Unfortunately, the pH* in both of these systems is different but this was because of solubility problems.

Reaction Between $(Et_3P)_2Au^+$ and Cystine (CysSSCys)

Figure 3 shows the ^{31}P NMR spectrum of 1 : 1 (0.01 M) solutions of CysSSCys and $(Et_3P)_2Au^+$ at pH* 12.5. Initially, the resonances at 44.0 and 34.6 ppm indicated a small quantity of mono compound formed and a relatively large quantity of bis compound remained unreacted. ^{31}P NMR spectra were initially recorded at small time intervals but no change was observed for any resonances. The figure also shows the spectrum of the same solution after 72 h. Reaction is complete, marked by intense resonances at 61.7 (Et_3PO) and 34.6 ppm (Et_3PAu^+). The resonance at 44.0 ppm disappears, showing that the $(Et_3P)_2Au^+$ is completely consumed. Note here again that no CysS–Au–PEt_3 species was detected.

Reaction Between $(Me_3P)_2Au^+$ and CymSeSeCym: Reaction B

In order to compare the reactivity of $(Et_3P)_2Au^+$ and $(Me_3P)_2Au^+$ with respect to breaking Se–Se and S–S bonds, the same series of reactions was carried out with $(Me_3P)_2Au^+$. First, $(Me_3P)_2AuBr$ was dissolved in the minimum amount of CD_3OD

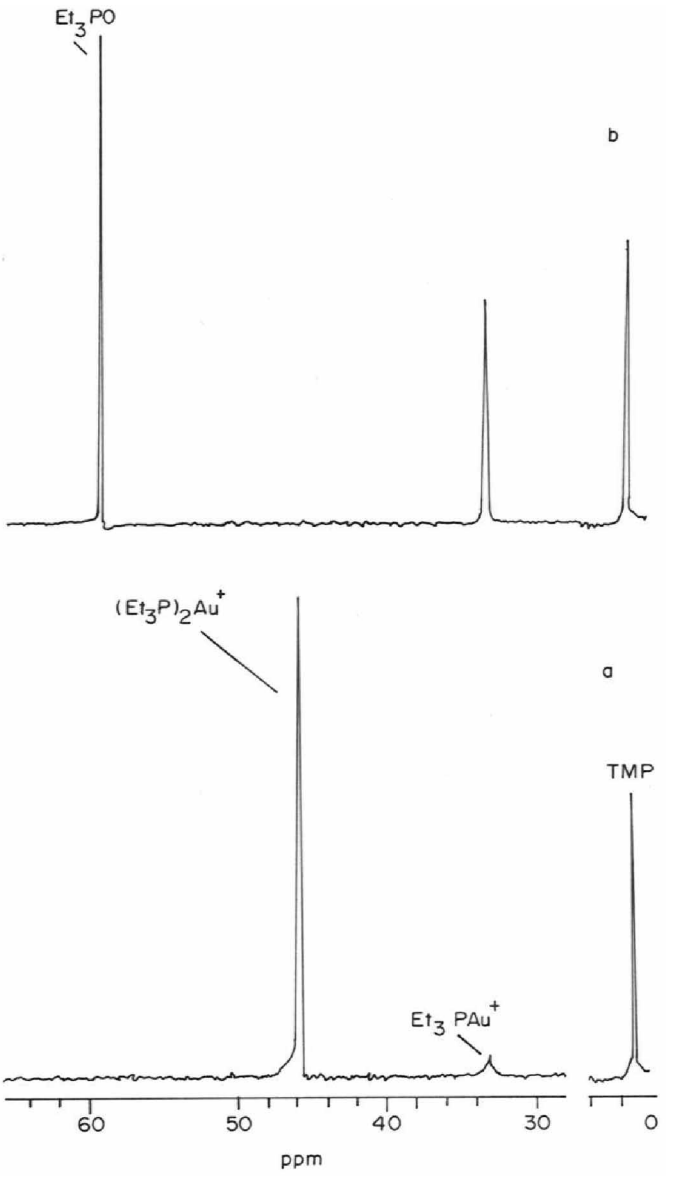

FIGURE 3 202.35 MHz $^{31}P\{^{1}H\}$ spectra of 0.01 M $(Et_3P)_2Au^+$: 0.01 M CysSSCys in D_2O after 10 min (lower) and 72 h (upper).

(1 to 2 drops) and the required amount of D_2O was added. Figure 4(a) shows the ^{31}P NMR spectrum of a reaction between $(Me_3P)_2AuBr$ and CymSeSeCym (1 : 1; 0.01 M) in D_2O at pH* 7.4. The reaction is almost instantaneous, indicated by resonances at −3.1 (Me_3PAu^+), 30.9 (Me_3PAu–SeCym), 50.1 (Me_3PO) and 4.3 ppm $(Me_3P)_2Au^+$. The resonance at 30.9 ppm disappears after 30 min (Fig. 4b), showing the low stability of Me_3PAu–SeCym. After 8 h (Fig. 4c) the spectrum shows the complete absence of the resonance at 4.3 ppm $(Me_3P)_2Au^+$, marking the completion of the reaction. A new resonance (of very low intensity) is observed as a triplet at −6.2 ppm, having a

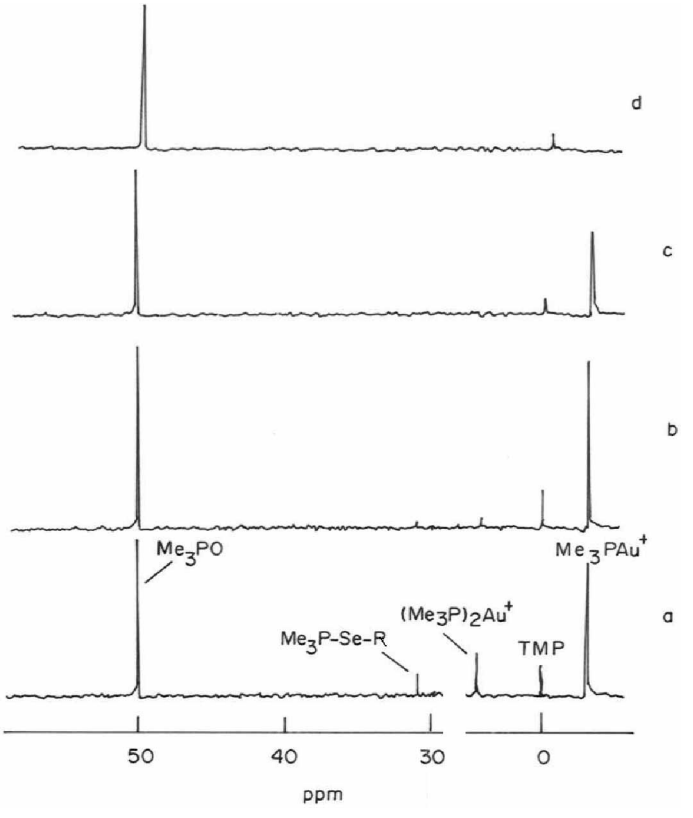

FIGURE 4 202.35 MHz $^{31}P\{^{1}H\}$ spectra of 0.01 M $(Me_3P)_2Au^+$: 0.01 M CymSeSeCym in D_2O at various time intervals; (a) 5 min, (b) 15 min, (c) 6 h, (d) 56 h.

coupling constant of 78 Hz throughout the reaction (not shown in the figure). However, after 56 h reaction (Fig. 4d) the triplet at −6.2 and the singlet at −3.1 ppm disappear.

Reaction Between Me_3P and CymSeSeCym

In order to explore the new resonance at −6.2 ppm observed in the above experiment, the following reaction was carried out. The CymSeSeCym solution was prepared in D_2O at pH* 7.2 and mixed with neat Me_3P. The ^{31}P NMR observed for the resulting solution showed a weak resonance as a triplet at 30.5 ppm with J coupling of 71 Hz, an intense resonance at 50.1 ppm (Me_3PO) and another weaker resonance at 39.13 ppm. This shows that the −6.2 ppm resonance is not due to $CymSePMe_3$.

Reaction Between $(Me_3P)_2Au^+$ and CymSSCym

The reaction between CymSSCym and $(Me_3P)_2Au^+$ was also followed by ^{31}P NMR over time. The solutions were made as described above at pH* 7.4 and the reaction was monitored for 48 h. A gradual decrease in the resonance intensity of $(Me_3P)_2Au^+$ at 4.3 ppm and an increase in the resonance intensity of Me_3PAu^+ at −3.1 ppm

TABLE II Second-order rate constants (k) measured for $(R_3P)_2Au^+$ in its reaction with disulfide or diselenide

Reactions	*pH**	k ($M^{-1}s^{-1}$)	*Ref.*
$(Et_3P)_2Au^+ + CymSeSeCym$	7.2	5.2×10^{-3}	This work
$(Me_3P)_2Au^+ + CymSeSeCym$	7.4	8.5×10^{-3}	This work
$(Me_3P)_2Au^+ + CymSSCym$	7.2	17.8×10^{-3}	This work
$(Et_3P)_2Au^+ + CymSSCym$	7.2	5.0×10^{-5}	This work
AuStm + RSe–Stm		3.21×10^{-4}	[11]

was observed, along with an increase in intensity for Me_3PO at 50.1 ppm. It is interesting to note that no CymS–Au–PMe_3 species was detected.

Verification of Et_3PAu–SeCym and Me_3PAu–SeCym Complexes

In order to verify the presence of $Et_3PAuSeCym$ and $Me_3PAuSeCym$ in reactions A and B above, two independent reactions were carried out. CymSeSeCym in D_2O at pH 7.4 was reduced by $NaBH_4$ [8]. The resulting solution was acidified with DCl to dissolve the formed turbidity and one equivalent of $(Et_3P)_2Au^+$ was added. A ^{31}P NMR spectrum recorded immediately showed a resonance at 59.21 ppm, corresponding to $Et_3PAuSeCym$, as identified earlier. A similar reaction was carried out with $(Me_3P)_2AuBr$ and the NMR spectrum showed a resonance at 31.97 ppm corresponding to $Me_3PAuSeCym$. A ^{31}P NMR signal for Me_3PSe was observed at 9.92 ppm, ruling out the possibility of its formation in any of the reactions with gold complexes.

Study of Reaction Kinetics

The rate constants, k, were determined for the reaction of $(Et_3P)_2Au^+$ and $(Me_3P)_2Au^+$ using the second-order rate equation, $1/x = kt + 1/x_0$ (Table II). The intensity of the phosphorus signal of $(Et_3P)_2Au^+$ was measured *vs* time, where x = intensity of $(Et_3P)_2Au^+$ at time t and x_0 = intensity of $(Et_3P)_2Au^+$ at $t = 0$. T_1 for $(Et_3P)_2Au^+$ is reported as 7.57 and 11.68 s in $(CD_3)_2SO$ and CH_3OD, respectively [9]. We used 60.0-s delay time for the kinetic measurements.

DISCUSSION

The cleavage of the disulfide bonds of bovine serum albumin and red blood cells with $(Et_3P)_2Au^+$ has been investigated by us and by Sadler *et al.* [6,7,10]. However, reduction of diselenide bonds with this complex has not been reported in the literature, although we recently studied reactions of these diselenides with Au(I)thiomalate (AuStm) by ^{13}C NMR spectroscopy [11]. Formation of R–Se–Au–PEt_3 by the cleavage of diselenide bonds and formation of Et_3PAu^+ for both CymSeSeCym and CysSeSeCys is confirmed by ^{31}P NMR spectroscopy.

Recently we reported the interactions of various thiones, including ergothionine and thiourea, with auranofin and Et_3PAuCl studied by ^{31}P NMR spectroscopy [12,13]. We noted that thiones which are weaker bases than thiols were able to replace both phosphine and thiolate ligands from the Au(I) of auranofin. For the first time we noted that minute amounts of Et_3P can react with thione to give Et_3PSR (phosphine sulphide where R = thiourea or thione). Similarly, an albumin–phosphonium

intermediate (iPr$_3$P$^+$SCH$_2$-(HSCH$_2$)albumin was observed in the reaction of iPr$_3$PAuCl with albumin by ^{31}P NMR spectroscopy [14]. However, there is no evidence of CymSePMe$_3$ species in these studies.

The fact that the new triplet at -6.2 ppm disappears when $(Me_3P)_2Au^+$ is consumed (Fig. 4) suggests that the phosphorus of this new resonance is bonded to $(Me_3P)_2Au^+$ and, somehow, RSeH binds to it forming $[(Me_3PAu)_2(SeCym)]^+$; this then dissociates to form other products: Me_3PO, Me_3PAu^+ and AuSeR. This assignment of $[(Me_3PAu)_2(SeCym)]^+$ is based on our previous studies, when albuminSAuPMe$_3$ reacted with Me_3PAuCl to give a (μ-thiolato)digold adduct of albumin with a signal at -12.7 ppm [15].

When $(R_3P)_2Au^+$ reacts with diselenides, $R_3PAuSeR$ is formed. However, disulfide reactions with $(R_3P)_2Au^+$ did not give any detectable intermediate (R_3PAuSR), which suggests that once disulfide bonds are broken the reaction proceeds rapidly.

Values of k are given in Table II. The case of CymSeSeCym with $(Me_3P)_2Au^+$ showed faster kinetics than $(Et_3P)_2Au^+$ in breaking the Se–Se linkage. In the reaction between CymSSCym and $(Me_3P)_2Au^+$, the k value is double that of CysSeSeCys. CymSeSeCym reacts with $(Et_3P)_2Au^+$ about 100 times faster than its corresponding disulfide. However, cystamine reacts twice as fast with $(Me_3P)_2Au^+$ as compared to its corresponding diselenide. It is of interest to note that $(Me_3P)_2Au^+$ is over 300 times more reactive with CymSSCym as compared to $(Et_3P)_2Au^+$. This observation indicates that $(Me_3P)_2Au^+$ breaks the disulfide bond much faster than $(Et_3P)_2Au^+$, indicating that $(Me_3P)_2Au^+$ is probably more toxic. This is perhaps one of the reasons auranofin contains Et_3PAuSR instead of Me_3PAuSR and $(Et_3P)_2Au^+$ has a similar biological activity to auranofin [7].

We recently reported the reaction of diselenides with AuStm. When AuStm reacted with diselenides it produced RSe–Stm (selenyl sulfide) species, which are unstable and the second order k measured was $3.21 \times 10^{-4}\,M^{-1}\,s^{-1}$ at 24°C [11]. We noted that diselenides react with AuStm faster than with disulfides [16].

The kinetics of symmetrical selenol/diselenides and thiol/disulfides have been investigated extensively by Rabenstein [17,18]. The rate constant for selenol/diselenides is 1.2×10^7 times faster than thiol/disulfides (where thiol and selenol = cysteamine/selenocysteamine) at pH* 7.4. This observation suggests that diselenides are very reactive compared to disulfides. Here we have demonstrated that disulfide and diselenide bonds can be reduced with $(R_3P)_2Au^+$ complexes. The rate constants show that diselenide is at least 100 times more reactive with $(Et_3P)_2Au^+$ than disulfide. It is also shown that $(Me_3P)_2Au^+$ is over 300 times more reactive with disulfide than the analogous $(Et_3P)_2Au^+$ species, indicating that $(Me_3P)_2Au^+$-containing drugs may be more toxic than those containing $(Et_3P)_2Au^+$.

Acknowledgments

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