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Formation, equilibrium properties and decomposition in aqueous solution of monoorganothallium(III) ions containing $RC(O)CH_2$ groups. Preparation of monoacetonylthallium(III) compounds

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Abstract

The reactions of thallium(III) with some ketones in the presence and absence of Cl^-, Br^-, CN^-, CH_3COO^- and CF_3COO^- ions in acidic aqueous solution, and the stabilities of the resulting monoorganothallium(III) species in solution have been examined. The rate-determining step in the formation of these compounds is the acid-catalyzed enolisation of the ketones. The formation reactions are reversible: the ketonyl groups can be exchanged by Cl^-, Br^-, CN^- and by other ketones. The equilibrium constant at 25 °C for the reaction:

$$H^+ + CH_3C(O)CH_2TlCl^+ + Cl^- \rightleftharpoons TlCl_2{}^+ + CH_3C(O)CH_3$$

in about 1 molar $HClO_4$ was found to be 780 (±160) M^{-1}. This unusual behaviour of the Tl^{III}-ketone systems can be accounted for by assuming that enolate complexes are present in low concentration, in equilibrium with the monoorganothallium(III) species. Two routes for decomposition of these species have been established. One of them takes place through $RCH_2C(O)CH_2Tl^{2+}$ ions and the other (when an excess of Cl^- is present) through $RCH_2C(O)CH_2TlCl^+$ ions. The latter results in formation of α-monochlorinated product with the composition $RCHClC(O)CH_3$ (where R = H, alkyl, aryl), probably via a five-ring enolate intermediate. Formation of diorganothallium(III) species of the type $[RC(O)CH_2]_2Tl^+$ has also been demonstrated. Some new solid monoorganothallium(III) compounds with the composition $ArC(O)CH_2TlCl_2$ ($Ar = C_6H_5$, $4'$-ClC_6H_4, $4'$-$CH_3C_6H_4$, $2'$-$C_{10}H_7$), $RC(O)CH_2$-$TlCl(NO_3)$ ($R = CH_3$, $(CH_3)_3C$) and $(CH_3)_3CC(O)CH_2Tl(S_2CNEt_2)_2$ have been

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prepared. ^{205}Tl NMR parameters for some mono- and di-organothallium(III) species are given.

Introduction

Monoarylthallium(III) compounds are usually stable and can be isolated without difficulty. Monoalkylthallium(III) compounds, on the other hand, are kinetically and thermodynamically unstable [1–4]. Some aliphatic monoorganothallium(III) carboxylates [5–9], cyanocarboxylates [10–13], and chelates have been prepared, but all of the very few known halogenides have an unsaturated carbon atom bonded to Tl [15,16] or thallium is connected to an aromatic [17,18] or $(CH_3)_3C$ group [19,20]. On the other hand, unstable non-isolable monoorgano-Tl^{III} compounds have often been postulated as intermediates in the oxythallation of olefins. These compounds undergo rapid decomposition to give products derived by oxidation of the organic group with simultaneous reduction of Tl^{III} to Tl^{I}. These reactions have become very important in organic synthesis during the last 15–20 years and as a consequence the chemistry of monoorganothallium(III) compounds has become important, too [2,21,22]. We previously found that relatively stable monoorgano compounds are formed in the reactions of ketones with different thallium(III) compounds in aqueous solution [23]. Because of the importance of monoorganothallium(III) compounds it is surprising that except for those involving chalcones and aryl alkyl ketones the reactions of Tl^{III} with ketones have remained almost unstudied [22]. Moreover, to our knowledge no organothallium(III) compound containing a group derived from a ketone has ever been prepared. We thus decided to make a more detailed study of these reactions. During this study we used concentrations of the reactants as high as normally used for preparative purposes and because of this the pH and ionic strength changed considerably as the reaction proceeded, and accordingly, the results must be regarded as only semi-quantitative from the kinetic point of view. Our work was focused on the rates of formation and decomposition of the monoorganothallium(III) compounds, and on the conditions leading to preparation of compounds of the type $RC(O)CH_2TlXY$.

Results and discussion

The reaction of Tl^{III} species with ketones and the decomposition of the monoorgano-Tl^{III} species formed were monitored by ^{205}Tl NMR spectroscopy, usually for 50–100 hours. The results for the first few hours of two typical runs are shown in Fig. 1. The rates of formation and decomposition of monoorganothallium(III) species are summarized in Table 1. Some selected formation curves for monoacetonylthallium(III) species are shown in Fig. 2.

Reaction with acetone

The rate of formation of monoacetonyl species (Table 1, Fig. 2) depends considerably on the acidity of the samples (cf. samples 2, 3 and 4, or 5–8), but not on the identity of the Tl^{III} reactant (cf. samples 3, 7, 9, 13–16). This is consistent with earlier results, showing that the rate-determining step in the reaction of Tl^{III} compounds with ketones is the acid-catalyzed enolisation of the ketones, which is

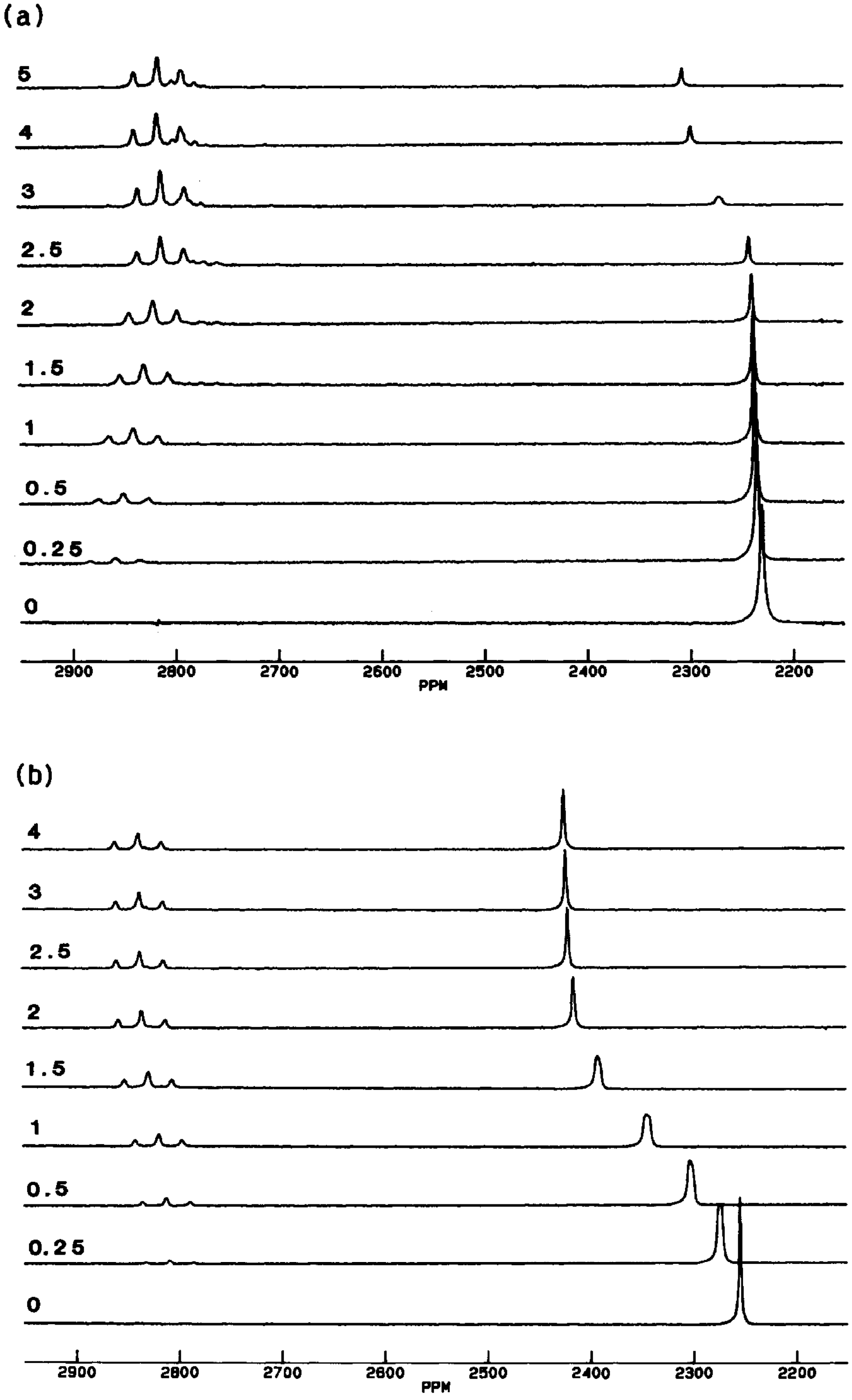


Fig. 1. Variation of the ^{205}Tl NMR spectrum with time during the first few hours (as indicated on the left side of the Figures) of the reaction of acetone with a solution of average composition (a) TlCl^{2+} and (b) $\mathrm{TlCl}_2{}^{+}$. The triplet at the high frequency is from monoacetonylthallium(III) species, while the singlet at the low frequency is from Tl(III) chloro complexes (TlCl_n^{3-n}).

Table 1

Rates of formation and decomposition of monoketonylthallium(III) compounds

No. and composition of samples, solvent	Yield (%) monoketonylthallium (III) at time (h) [a]											Maximum yield of species (%/h) [a]	Decomposition (%/h) [b]
	0.25	0.5	1	1.5	2	2.5	3	4	5	6	7		
1 Tl/Cl/$HClO_4$/MeC(O)Me,H_2O = 1/0/2.2/1 [c]	8	15	22	27	32							32/2	38
2 Tl/Cl/$HClO_4$/MeC(O)Me,H_2O = 1/1/1.2/1	6	9	15	19	24	28	31	36	37	39	34	39/6	3.9
3 Tl/Cl/$HClO_4$/MeC(O)Me,H_2O = 1/1/2.2/1	10	19	32	44	53	61	66					67/3.3	5.6
4 Tl/Cl/$HClO_4$/MeC(O)Me,H_2O = 1/1/3.9/1	30	49	69	78								78/1.5	7.3
5 Tl/Cl/$HClO_4$/MeC(O)Me,H_2O = 1/2/0.2/1	–	–	3	5	6	8	9	12	14	17	20	37/14	0.38
6 Tl/Cl/$HClO_4$/MeC(O)Me,H_2O = 1/2/1.2/1	4	9	18	24	29	33	35					38/4	0.47
7 Tl/Cl/$HClO_4$/MeC(O)Me,H_2O = 1/2/2.2/1	11	19	30	37	40							41/2.2	0.65
8 Tl/Cl/$HClO_4$/MeC(O)Me,H_2O = 1/2/4.0/1	23	42	46									46/1	8.2
9 Tl/Cl/$HClO_4$/MeC(O)Me,H_2O = 1/3/2.2/1	8	12	13									13/1	0.14
10 Tl/Cl/$HClO_4$/MeC(O)Me,H_2O = 0.5/0.5/1.1/1	9	17	32	46	58	70	83					88/3.5	1.2
11 Tl/Cl/$HClO_4$/MeC(O)Me,H_2O = 1/1/2.2/2	19	37	71	82								82/1.5	2.7
12 Tl/Cl/$HClO_4$/MeC(O)Me,S [d] = 0.5/0.5/1.1/0.5	10	18	30	41	50	58	66	78	86	89		89/6	2.3
13 Tl/Br/$HClO_4$/MeC(O)Me,H_2O = 1/1/2.2/1	9	18	35	51	67	79	82					82/3	8.7
14 Tl/CN/$HClO_4$/MeC(O)Me,H_2O = 1/2/2.2/1	8	16	33	46	58	67	75	86				89/4.7	1.8
15 Tl/CH_3COO/$HClO_4$/MeC(O)Me,H_2O = 1/3/2.2/1	4	9	18	26	33	40	48	61	68	75	78	83/9	4.3
16 Tl/CF_3COO/$HClO_4$/MeC(O)Me,H_2O = 1/3/2.2/1	7	14	27	39	51	61	69	74	78			78/5	3.9
17 Tl/Cl/$HClO_4$/EtC(O)Me,H_2O = 1/1/2.2/1	6	12	16	20								20/1.5	29
18 Tl/CN/$HClO_4$/CH_2=CHC(O)Me,H_2O = 1/3/0.2/1	4	8	14	20	24	28	31	36	39	41	43	44/9	0.36
19 Tl/Cl/$HClO_4$/$Me_3CC(O)Me$,S = 0.5/0/1.1/0.5	3	5	9	14	18	21	24	29	33	36	39	54/15	2.2
20 Tl/Cl/$HClO_4$/$Me_3CC(O)Me$,S = 0.5/0.5/1.1/0.5	3	6	13	19	25	31	37	46	53	59	64	83/15	0.48
21 Tl/CN/$HClO_4$/$Me_3CC(O)Me$,S = 0.5/1/1.1/0.5	3	6	12	17	22	26	31	39	46	51	56	81/42	–
22 Tl/Cl/$HClO_4$/PhC(O)Me,S = 0.5/0.5/1.1/0.5	4	7	13	18	22	25	29	35	39	44	47	67/17	0.67
23 Tl/Cl/$HClO_4$/4′-ClPhC(O)Me,S = 0.5/0.5/1.1/0.5	2	3	6	9	11	13	16	19	23	26	29	50/24	0.41
24 Tl/Cl/$HClO_4$/4′-MeOPhC(O)Me,S = 0.5/0.5/1.1/0.5	2	4	6	8	10	12	14	17	20	22	24	31/13	2.6
25 Tl/Cl/$HClO_4$/2′,4′,6′-$Me_3PhC(O)Me$,S = 0.5/0.5/1.1/0.5	3	5	10	16	21	26	31	40	48	56	63	83/14	0.30
26 Tl/Cl/$HClO_4$/2′-$C_{10}H_7C(O)Me$,S = 0.5/0.5/1.1/0.5	3	5	9	13	16	19	21	26	30	35	39	51/15	1.4

[a] Relative to the total amount of Tl in the sample. [b] i.e. percentage of the monoketonylthallium(III) species decomposed per hour after the maximum yield indicated in the preceding column has been reached. [c] The numbers denote concentrations in mole/l. [d] S = mixture of H_2O and CH_3CN in 1/1 mole ratio.

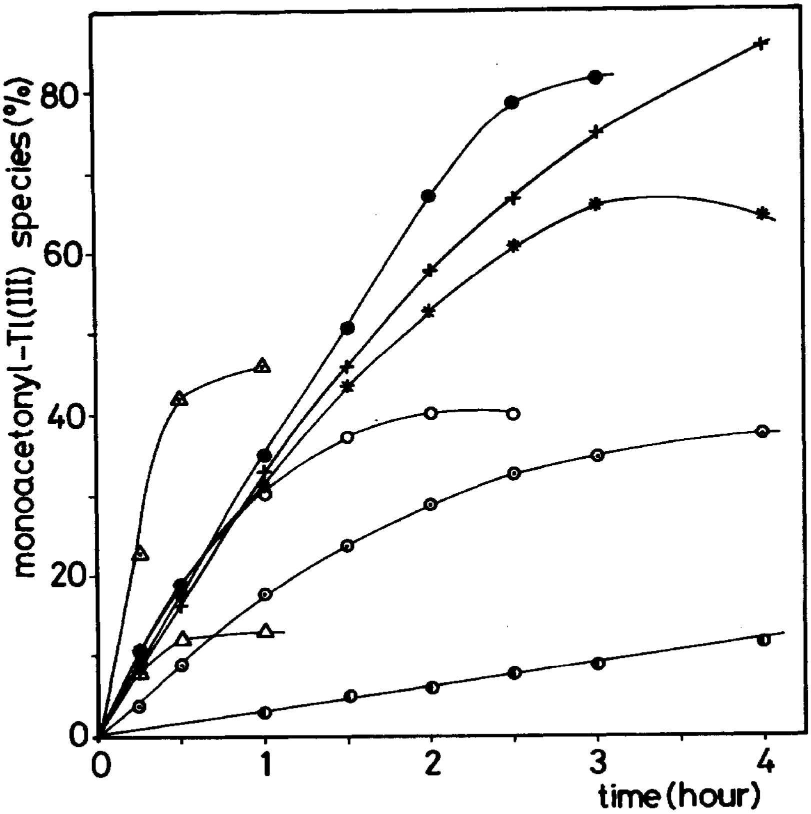


Fig. 2. Some formation curves for monoacetonylthallium(III) species as observed for sample 3 (*), 5 (◐), 6 (⊙), 7 (○), 8 (▲), 9 (△), 13 (●) and 14 (+).

followed by the oxythallation of the enols [24–26]. (The lower rate of formation in the case of $Tl(OOCCF_3)_3$ and $Tl(OOCCH_3)_3$ can be explained in terms of the buffer effect and/or the effect of the bulk on trifluoroacetate and acetate ions).

During the reaction in a solution with an average composition $TlCl^{2+}$ (i.e. $Tl^{III}/Cl_{tot} = 1/1$) there is only a little change in the chemical shift of the resonance from unchanged Tl^{III} species (Fig. 1a). In contrast, when a $TlCl_2{}^+$ solution is used the ^{205}Tl NMR signal of the unreacted Tl^{III} species is shifted markedly to higher frequencies (Fig. 1b), indicating a progressive increase in the coordination number of the $TlCl_n{}^{3-n}$ complexes. A chemical shift of 2425 ppm corresponds to an average composition $TlCl_3$ [27]. This means that the monoacetonylthallium(III) product is present mainly in the form of $CH_3C(O)CH_2TlCl^+$ ion. Similar results were obtained in the case of $TlCl_3$. Thus, the formation of monoacetonyl compounds can be represented as in eq. 1.

$$CH_3C(O)CH_3 + 2\,TlCl_n^{3-n} \rightleftharpoons CH_3C(O)CH_2TlCl^+ + TlCl_{2n-1}^{4-2n} + H^+ \qquad (1)$$
(where $n = 1$–3)

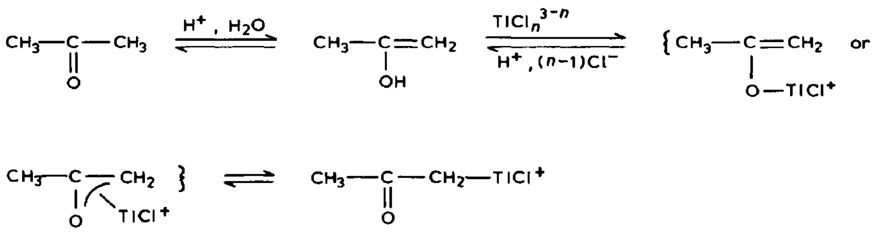
The increase in the coordination number of the inorganic chlorothallium(III) complexes leads to deactivation of some of the Tl^{III} reagent through formation of $TlCl_3$ and $TlCl_4{}^-$ complexes. This is reflected in the sharp decrease in the maximum yield of $CH_3C(O)CH_2TlCl^+$ ion as the ratio Cl^- to Tl^{III} is increased (cf. sample 3, 7 and 9, Table 1). Moreover, if NaCl is added to sample 3 in 1/1 or 2/1 ratio at the time when the maximum concentration of $CH_3C(O)CH_2TlCl^+$ is present, the quantity of the latter decreases from 67% to about 43 and 15%, respectively, of the total thallium during 5–10 minutes (cf. samples 7 and 9, Table 1). This shows that in the monoorganothallium compound the Cl^- ion is able to replace the $CH_3C(O)CH_2$ group, and so the latter behaves like a normal ligand. In order to obtain a more quantitative picture of this equilibrium behaviour we determined the equilibrium constant at 25 °C for reaction 2. This was done in the following way. First an

$$H^+ + CH_3C(O)CH_2TlCl^+ + Cl^- \rightleftharpoons TlCl_2^+ + CH_3C(O)CH_3 \qquad (2)$$

aqueous solution with the composition $Tl/Cl/HClO_4/\text{acetone} = 0.038/0.038/0.91/0.039$ molar was prepared. Low concentrations of the reacting species were used in order to keep the activity coefficients constant, and the 0.91 M perchloric acid served as the ionic medium. The formation of the monoorganothallium(III) species (reaction 1) was monitored by measuring ^{205}Tl NMR integrals of the signals of the inorganic and of the organic species, respectively. The decomposition of the monoorganothallium(III) compound was monitored by chemical analysis and by recording of the ^{205}Tl NMR spectra. After a few hours, when the formation and the decomposition reactions were negligibly slow compared to reaction 2, the ^{205}Tl NMR spectrum for the solution was recorded and the integrals of the inorganic and the organic signals were measured. The hydrogen ion concentration $[H^+]$ was determined by titration with NaOH, and was practically the same as at the start. The free acetone concentration was taken to be $\{[\text{acetone}]_{tot} - [CH_3C(O)CH_2\text{-}TlCl^+]\}$. In order to determine the remaining concentrations necessary for calculation of the equilibrium constant, namely $[TlCl_2{}^+]$ and $[Cl^-]$, the values of the stability constants for the different $TlCl_n{}^{3-n}$ complexes in the actual ionic medium were needed and thus were calculated by use of the specific interaction theory in the way described in ref. 28, and values of log β_n of 6.69, 11.79, 14.56, 16.43, for $n = 1$, 2, 3, and 4, respectively, were obtained. The equilibrium constant for reaction 2 could now be calculated and was found to be 720 M^{-1}.

Subsequently, a known amount of solid NaCl was added. After about 30 minutes the solution had reached chemical equilibrium and the value of the equilibrium constant for reaction 2 was again determined, and found to be 840 M^{-1}, in agreement with the previous value of 720 when the uncertainty in the peak integrals is taken into account.

This type of equilibrium behaviour of an organometallic species is unusual, but it has been found previously in the case of Hg^{II}-ethylene [29a] and Ag^{I}-ethylene [29b] systems. The reversibility of the formation of $CH_3C(O)CH_2TlCl^+$ ion can be explained by assuming an equilibrium between the σ-bonded organometallic species and the σ- or π-bonded enolate complex. The sequence for formation of the monoorganothallium compound from $TlCl_n{}^{3-n}$ and acetone is summarized in eq. 3:



(3)

The equilibrium properties of the Tl^{III}–Cl^-–acetone system are also evident when N_2 is bubbled through a solution with the composition $Tl^{III}/Cl/HClO_4/$acetone = 1/1/2.2/3.4. The percentage of $CH_3C(O)CH_2TlCl^+$ of the total thallium is 96.5 at the beginning of this experiment, (the rest is $TlCl_n^{3-n}$) but falls to 84, 76 and 61%, respectively, after 0.5, 2 and 7 h of the bubbling, and the concentration of $TlCl_n^{3-n}$ increases at the same time.

When Br^- is used instead of Cl^- the ^{205}Tl NMR signal of the inorganic thallium is shifted to lower frequencies, showing formation of $TlBr_2^-$ [27]. However, when CN^-, CH_3COO^-, or CF_3COO^- are used instead of Cl^- there is no change in the chemical shift of the unchanged TlX_n^{3-n} species. In spite of this, it is probable that these ligands are also coordinated in the $CH_3C(O)CH_2TlX^+$ species. An explanation may be that the corresponding higher $TlX_n^{(3-n)+}$ complexes are not formed in the very acidic medium because the undissociated acid HX competes for the X^- ions. In the case of the Tl^{III}–CN^- system (which is currently being examined in this laboratory [30]) the $TlCN_n^{3-n}$ complexes with $n > 2$ are much less stable than those with $n = 1, 2$.

Reaction with higher ketones

In the case of 2-butanone the rate of the formation is close to that for acetone, but the stability of the monoorgano species is much lower (sample 17, Table 1). Reactions between the ketones 2-pentanone and cyclohexanone with solutions of the composition "$TlCl^{2+}$" or "$Tl(OOCCH_3)_3$" are very fast, but the ^{205}Tl NMR signal of corresponding organothallium(III) species cannot be seen at all because of their low stability. With 2-pentanone, 70% of the Tl^{III} is reduced in 1.5 h for a solution with $Tl^{III}/Cl/HClO_4/$2-pentanone = 1/1/2.2/1. During similar reaction with cyclohexanone only the $TlCl_n^{(3-n)}$ signal is present in the NMR spectra 2 min after mixing the reactants. After 5 min this signal disappears completely and no other Tl^{III} signal is present, indicating a very fast redox reaction. For a solution with $Tl^{III}/CN/HClO_4/$cyclohexanone = 1/3/0.2/1 the reduction of Tl^{III} (which is present in solution mainly as $Tl(CN)_3$) is much slower, but in this case also the signal of the organothallium(III) cannot be observed.

Acetylacetone reacts very rapidly (the reaction is complete within one minute) at $Tl^{III}/Cl/HClO_4/$acetylacetone = 1/1/2.2/1 ratio. A ^{205}Tl-^1H doublet (at 2452 ppm) shows that one of the hydrogens at C(3)-carbon is replaced by $TlCl^{2+}$, which is what would be expected in view of the high acidity of these protons. During the rather fast decomposition of the product a triplet appears (at about 2690 ppm) showing a slow change of the thallation site from C(3) atom to C(1) atom, possibly for steric reasons. A similar result was obtained with $Tl^{III}/CN/HClO_4/$acetylacetone = 1/4/0.6/1. On the other hand, when acetylacetone was added to a solution of $CH_3C(O)CH_2TlCl^+$ only the triplet from $CH_3C(O)CH_2C(O)CH_2TlCl^+$ appeared (simultaneously with reduction of Tl^{III}) showing that the $[CH_3C(O)]_2CH$ group cannot replace $CH_3C(O)CH_2$ in the monoorganothallium(III) compound.

Reactions of t-butyl methyl ketone, various acetophenones, and 2′-acetonaphtone with $TlCl^{2+}$ are much slower in a 1/1 mixture of CH_3CN and water than those with acetone (Table 1). Chalcone reacts much more rapidly; more than 90% of thallium(III) being reduced within 3 h. No ^{205}Tl NMR signal from the organothallium(III) could be seen in this case. (For comparison, the reaction with acetone was also studied in 1/1 CH_3CN/water mixture, cf. Table 1.)

In the course of the reaction of $TlCl_2^+$ with t-butyl methyl ketone and acetophenone the shift of the ^{205}Tl NMR signal of the unchanged species was the same as that observed in the similar reaction with acetone. These systems also show reversible behaviour when NaCl is added, indicating that the reactions also follow the route shown in eq. 2. Another item of evidence for the reversible behaviour of ketone/Tl^{III}/Cl^- systems is that $(CH_3)_3CC(O)CH_2$ is partly replaced by $CH_3C(O)CH_2$ when acetone is added to a solution of $(CH_3)_3CC(O)CH_2TlCl^+$ ClO_4^-. Adding acetone to a solution with Tl^{III}/Cl/$HClO_4$/t-butyl methyl ketone = 1/1/2.2/2 at a time when the maximum concentration of the monoorganothallium(III) has been reached results in replacement of about 90% of $(CH_3)_3CC(O)CH_2$ in 2 h (Tl^{III}/acetone = 1/4). Similar exchange reactions takes place until the equilibrium ratio is reached when t-butyl methyl ketone is added to an aqueous solution of $CH_3C(O)CH_2TlCl^+$ ClO_4^-.

Formation of diketonylthallium(III) species

It is well established that the number of known diorganothallium(III) compounds and their stabilities are much higher than those of monoorganothallium(III) species [1,3,4]. However, during our investigations we observed formation of diorganothallium(III) only in a few cases. When strongly coordinating inorganic ligands (Cl^-, Br^-, CN^-) were present, diorganothallium(III) species appeared only in very low concentration (if at all) even when a high ketone to thallium(III) ratio was used; e.g., at Tl^{III}/Cl/$HClO_4$/acetone = 1/1/2.1/10, only 3–4% of the Tl^{III} was in the form of diorganothallium(III).

On the other hand, in the Tl^{III}–ClO_4^--acetone system, where no strongly coordinating ligands are present, the concentration of diorganothallium(III) is quite high; e.g., in sample no. 1 (Table 1) after 2 h as much as 20% of organothallium(III) was found as diorganothallium(III), and this percentage increases substantially at higher acetone/thallium(III) ratios. The concentration of $[CH_3C(O)CH_2]_2Tl^+$ drops to well below 3% of the total thallium(III) if HNO_3 is used instead of $HClO_4$. This shows that even the poorly coordinating NO_3^- ion can replace $CH_3C(O)CH_2$ groups effectively.

In the system with Tl^{III}/CH_3COO/$HClO_4$/acetone = 1/3/2.2/2, concentration of diorganothallium(III) species reaches 62% of the total organothallium(III). This compound begins to form when all the inorganic thallium(III) has been transformed to monoorganothallium(III) (Fig. 3). This behaviour is consistent with the rate-determining step for reaction 1 being the acid-catalyzed enolisation of acetone. Moreover, it shows that the reaction of the enol with $Tl(OOCCH_3)_n^{(3-n)^+}$ is much faster than that with the monoorganothallium(III) species. Increasing the acetone to thallium(III) ratio increases to the amount of diorganothallium(III) species formed. Bubbling nitrogen through the sample causes evaporation of acetone and so lowers the diorganothallium(III) concentration.

Diorganothallium(III) species are formed until an equilibrium concentration is reached when water is added to a THF solution of $C_6H_5C(O)CH_2TlCl_2$. The amount of this species increases as the water/THF ratio increases, and reaches 55% of the total organothallium(III) at THF/H_2O 1/0.53. Presumably, the following equilibrium exists:

$$2\,C_6H_5C(O)CH_2TlCl_2 \overset{THF/H_2O}{\rightleftharpoons} [C_6H_5C(O)CH_2]_2Tl^+ + TlCl_4^- \qquad (4)$$

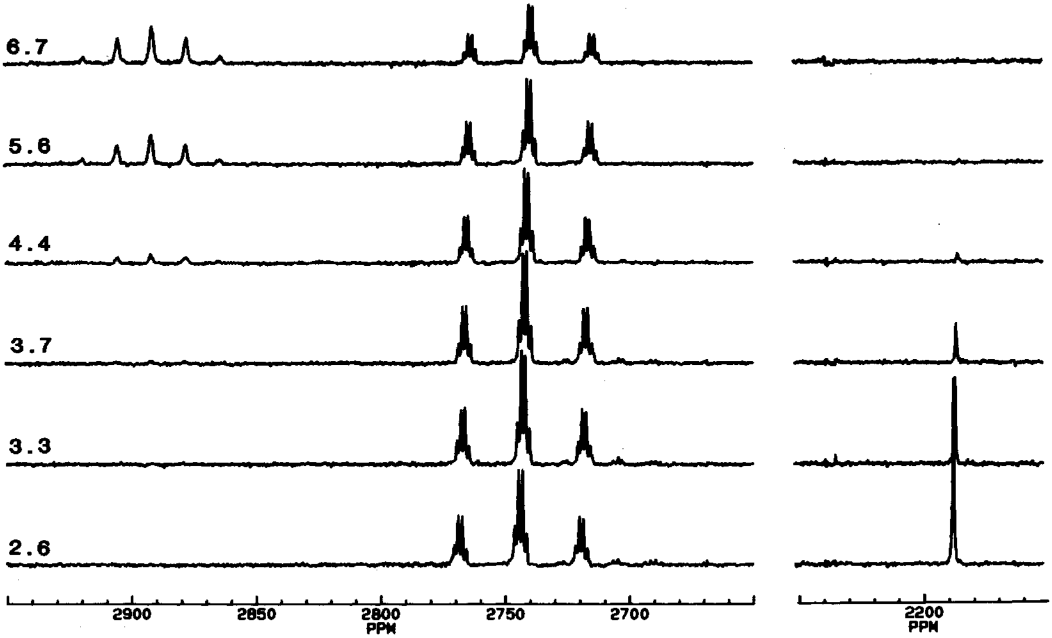


Fig. 3. Variation of the ^{205}Tl NMR spectrum with time (in hours; indicated on the left side of the figure) for an aqueous solution with $Tl^{III}/CH_3COO^-/HClO_4$/acetone = 1/3/2.2/2.

Side reactions

In the case of Cl^- or CN^- (denoted by X^-) containing samples with acetone, along with signals from the $CH_3C(O)CH_2TlX^+$ ions, signals from other species appear in ^{205}Tl NMR spectra as the reaction proceeds. The concentration of the latter is always lower than 5% of the total thallium in the sample, but is higher in samples with low acid concentration and increases considerably when the $TlX_n^{(3-n)+}$ to acetone ratio (n = 1,2) is raised progressively from 1/1 to 3/1. Among these low concentration species the most interesting one, which gives a doublet of triplets of triplets in ^{205}Tl NMR spectra, is believed to be a binuclear $XTlCH_2C(O)CH_2TlX^{2+}$ ion. Its (^{205}Tl–^{203}Tl) spin–spin coupling constant is 8020 Hz for $X = Cl^-$ and 5620 Hz for $X = CN^-$. Only a few organothallium(III) compounds with two thallium atoms have been reported in the literature [31–33]. Another low concentration species, represented by triplet of triplets in the ^{205}Tl NMR spectra, appears especially in solutions containing the CN^- ion. For this species we propose the formulation $XCH_2C(O)CH_2TlX^+$. There are two other minor species, one represented by doublet of quartets and the other one by doublet of doublets. The first one appears along with the monoorganothallium((III) compound. The second is characteristic of samples with the ratio $Tl^{III}/X^- = 1/1$, and appears as the monoorganothallium(III) decomposes.

Decomposition of monoketonylthallium(III) compounds

We have not examined in detail the chemistry of the decomposition of monoorganothallium(III) species. Only the effects of the type of ketone, the acid concentration, and the nature and concentration of the anion have been studied.

In several cases a precipitate is formed as the monoorganothallium(III) ion decomposes. This precipitate is the white $TlClO_4$ when the Cl^-/Tl^{III} ratio is ≤ 1, and the yellow $Tl^I{}_3Tl^{III}Cl_6$ when the ratio is > 2.

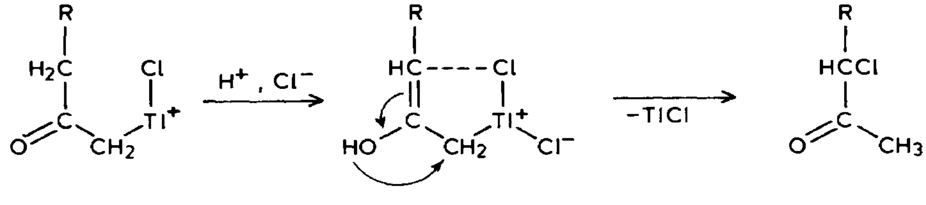
The anions (X^-) examined stabilize the $CH_3C(O)CH_2TlX^+$ species in the order $ClO_4^- \ll CH_3COO^- < CF_3COO^- < Br^- < CN^- < Cl^-$ (Table 1), which seems to correspond with the order of complex-forming ability of the anions, except for Br^- in strongly acidic media. Since $TlBr_n{}^{3-n}$ complexes are extremely stable, the reason for this behaviour is that there is probably some competing process, such as precipitation of the sparingly soluble $Tl^I{}_3Tl^{III}Br_6$ or bromination of the ketone. Decomposition of monoorganothallium(III) compounds is believed to occur through decomposition of dicoordinated $RTlX^+$ ions even when X^- is a poorly coordinating ligand such as $NO_3{}^-$, $BF_4{}^-$, $ClO_4{}^-$ or $SO_4{}^{2-}$ [22]. However, our investigation has revealed a sharp decrease in the rate of decomposition of acetonylthallium(III) species as the Cl^-/Tl^{III} ratio increases (see samples 1, 3, 7 and 9 in Table 1), which indicates that although the dominating species in aqueous solution is $RTlX^+$, RTl^{2+} may be the decomposing species, i.e.

$$\begin{array}{l} CH_3C(O)CH_2TlCl^+ \rightleftharpoons CH_3C(O)CH_2Tl^{2+} + Cl^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\downarrow \\ \qquad\qquad\qquad\qquad \text{decomposition products} \end{array} \tag{5}$$

The acidity of the solution does not significantly affect the rate of decomposition in the range $1.2 < [H^+] < 3.9$ mole/l for the $Tl^{III}/Cl = 1/1$ (samples 2–4 in Table 1) and $0.2 < [H^+] < 2.2$ mole/1 for $Tl^{III}/Cl = 1/2$ (samples 5–7 in Table 1), but the rate is considerably higher at $[H^+] = 4$ mole/l for $Tl^{III}/Cl = 1/2$ (sample 8, Table 1); we cannot suggest a satisfactory explanation for the latter observation. The number of the examined ketones is not enough to define the relationship between the structure of a ketone and the stability of the appropriate monoorganothallium(III) species, but the monoorganothallium(III) derivatives of t-butyl methyl ketone and of aryl methyl ketones are more stable than the acetonyl compound. Also, compounds containing a CH_2 group on one or both sides of the CO group are very unstable.

Our preliminary studies of the decomposition when $Tl(ClO_4)_3$ or $TlCl(ClO_4)_2$ is used (when the reaction follows eq. 5) show that about two thirds of the acetone or t-butyl methyl ketone are regenerated at a Tl^{III}/ketone ratio of 1/1 and several different products of the oxidation of ketones are formed. This means that roughly six-electron oxidation takes place. Formation of α-ketonyl compounds of the type $RC(O)CH_2Tl(NO_3)_2$ during solvothallation of $RC{\equiv}CH$ has been postulated; these compounds decompose by four-electron oxidation and RCOOH and CH_2O are formed [21].

Another type of redox reaction occurs at higher Cl^-/Tl^{III} ratios. This reaction is much slower than that discussed above, and gives monochlorinated ketones in which the chlorination site is not the same as the thallation site [23]. To account for this result the process shown in eq. 6, occurring via a five-ring enolate intermediate, is proposed.



(6)

Preparation of solid monoketonylthallium(III) compounds

Monoorganodichlorothallium(III) compounds can be isolated as crystals if CH_3CN is removed by bubbling N_2 through samples 22, 23 or 26 at the time the maximum yield is reached (cf. Table 1). $C_6H_5C(O)CH_2TlCl_2$ precipitates out after 2–6 days from samples $Tl^{III}/Cl^-/HClO_4$/acetophenone = 1/1–2/0.2–2.2/1 and $Tl^{III}/Cl^-/CN^-/HClO_4$/acetophenone = 1/1/1/2.2/1 when water is used instead of H_2O/CH_3CN mixtures. In these cases the acetophenone extracts Tl^{III} from the aqueous phase and the reaction takes place in the organic phase. (When $Tl(ClO_4)_3$ is used in the reaction with acetophenone i.e. $[Cl^-] = 0$, phenyl-acetic acid is formed at high yield as a consequence of aryl migration, which is characteristic of solvothallation derivatives of aryl alkyl ketones [34].) The monoketonylthallium(III) compounds $C_6H_5C(O)CH_2TlCl_2$ and 4'-$CH_3C_6H_4C(O)CH_2TlCl_2$ are formed at high yield according to eq. 7.

$$Tl_2O_3 + 2\ ArC(O)CH_3 + 4\ HCl \xrightarrow{H_2O-CH_3CN} 2\ ArC(O)CH_2TlCl_2 + 3\ H_2O \qquad (7)$$
$$(Ar = C_6H_5,\ 4'\text{-}CH_3C_6H_4)$$

Some reaction takes place with 2',4',6'-$(CH_3)_3C_6H_2C(O)CH_3$ also (i.e. Tl_2O_3 disappears) but no pure product could be isolated. $C_6H_5C(O)CH_2TlCl_2$ slowly decomposes at room temperature with formation of $C_6H_5C(O)CH_2Cl$ and TlCl; the reaction is almost complete within three months.

Attempts to separate $CH_3C(O)CH_2TlCl^+\ X^-$ and $(CH_3)_3CC(O)CH_2TlCl^+\ X^-$ (where X = BF_4, ClO_4, PF_6, SbF_6, and $B(C_6H_5)_4$) were unsuccessful. With $NaB(C_6H_5)_4$ a precipitate was formed, but it was not the desired salt. On the other hand, appropriate nitrate salts could be separated in relatively pure form by extraction with THF from the solid residue obtained by neutralization and evaporation of samples obtained from a $Tl^{III}/Cl/HNO_3$/ketone ratio of 1/1/2.2/1 samples. The compound $(CH_3)_3CC(O)CH_2TlCN^+\ NO_3^-$ could not be extracted by THF or CH_3CN from the residue of a similar reaction.

In the course of attempts to prepare $RC(O)CH_2Tl(SSCNEt_2)_2$ it was found that diethyl dithiocarbamate partially replaced $RC(O)CH_2$ groups (R = CH_3, $(CH_3)_3C$) and not Cl^- ligands in monoketonyl monochlorothallium(III) species. Replacement of $(CH_3)_3CC(O)CH_2$ group is much less pronounced in a sample containing acetate with $Tl^{III}/CH_3COO^-/HClO_4$/ t-butyl methyl ketone = 1/3/2.2/1. In this case the desired complex could be separated relatively pure.

During neutralization of aqueous solutions containing $CH_3C(O)CH_2TlCl^+$ a yellowish-red solution is formed at pH 3–6. Addition of CH_3CN to this solution causes separation of a yellowish-brown solid. A yellowish-brown solid separates immediately when a solution containing $(CH_3)_3CC(O)CH_2TlCl^+\ NO_3^-$ is neutralized. Most of this material can be dissolved in diethyl ether and precipitated from this solution by addition of hexane. According to the Tl^{III} and chloride analyses and ^{205}Tl NMR spectra of solutions obtained by dissolving the solids in aqueous $HClO_4$, these materials seem to have the composition $[RC(O)CH_2TlCl]_2O$, where R = CH_3 or $(CH_3)_3C$. Since e.g. CH_3TlO is a known species [10], we have also tried to prepare the RTlO-type compound with R derived from t-butyl methyl ketone by neutralization of a mixture obtained from a Tl^{III}/acetate/ $HClO_4$/ t-butyl methyl ketone ratio of 1/3/2.2/1 about 65 h after mixing the reactants, but the solid

Table 2. Some ^{205}Tl NMR parameters of ketonylthallium(III) compounds

Species	Sample composition (solvent) [a]	δ (ppm)	^2J(H–Tl) (Hz)	^4J(H–Tl) (Hz)
MeC(O)CH$_2$Tl^{2+}	Tl/HClO$_4$/MeC(O)Me = 1/2.2/1(H$_2$O)	2880	1292	135
MeC(O)CH$_2$TlNO$_3$$^+$	Tl/HNO$_3$/MeC(O)Me = 1/2.2/1(H$_2$O)	2706	1472	73
MeC(O)CH$_2$TlCl$^+$	MeC(O)CH$_2$TlClNO$_3$(H$_2$O)	2735	1270	–
MeC(O)CH$_2$TlCl$^+$	Tl/Cl/HClO$_4$/MeC(O)Me = 1/1/2.2/1(H$_2$O)	2860	1185	73
MeC(O)CH$_2$TlCl$^+$	Tl/Cl/HNO$_3$/MeC(O)Me = 1/1/2.2/1(H$_2$O)	2692	1290	51
MeC(O)CH$_2$TlClNO$_3$	THF	2741	1226	–
[MeC(O)CH$_2$]$_2$Tl$^+$	Tl/HClO$_4$/MeC(O)Me = 1/2.2/1(H$_2$O)	2938	701	–
[MeC(O)CH$_2$]$_2$Tl$^+$	Tl/MeCOO/HClO$_4$/MeC(O)Me = 1/3/2.2/1(H$_2$O)	2888	717	–
MeC(O)CH$_2$TlBr$^+$	T/Br/HClO$_4$/MeC(O)Me = 1/1/2.2/1(H$_2$O)	2570	1111	–
MeC(O)CH$_2$TlCN$^+$	Tl/CN/HClO$_4$/MeC(O)Me = 1/2/2.2/1(H$_2$O)	2818	1048	68
MeC(O)CH$_2$TlOOCMe$^+$	Tl/MeCOO/HClO$_4$/MeC(O)Me = 1/3/2.2/1(H$_2$O)	2749	1268	84
MeC(O)CH$_2$TlOOCCF$_3$$^+$	Tl/CF$_3$COO/HClO$_4$/MeC(O)Me = 1/3/2.2/1(H$_2$O)	2845	1389	–
ClTlCH$_2$C(O)CH$_2$TlCl^{2+}	Tl/Cl/HClO$_4$/MeC(O)Me = 1/1/2.2/0.5(H$_2$O)	2754	1203	65
NCTlCH$_2$C(O)CH$_2$TlCN^{2+}	Tl/CN/HClO$_4$/MeC(O)Me = 1/2/2.5/1(H$_2$O)	2776	1113	70
EtC(O)CH$_2$TlCl$^+$	Tl/Cl/HClO$_4$/EtC(O)Me = 1/1/2.2/1(H$_2$O)	2822	1175	–
MeC(O)CH=CHTlCN$^+$	Tl/CN/HClO$_4$/CH$_2$=CHC(O)Me = 1/3/0.2/1(H$_2$O)	2698	–	–
Me$_3$CC(O)CH$_2$Tl^{2+}	Tl/HClO$_4$/Me$_3$CC(O)Me = 0.5/1.1/0.5/S [b]	2918	1194	–
Me$_3$CC(O)CH$_2$TlCl$^+$	Me$_3$CC(O)CH$_2$TlClNO$_3$(H$_2$O)	2804	1135	–
Me$_3$CC(O)CH$_2$TlCl$^+$	Tl/Cl/HClO$_4$/Me$_3$CC(O)Me = 0.5/0.5/1.1/0.5(S)	2872	1053	–
Me$_3$CC(O)ch$_2$TLCN$^+$	Tl/CN/HClO$_4$/Me$_3$CC(O)Me = 0.5/1/1.1/0.5(S)	2856	986	–
Me$_3$CC(O)CH$_2$TlOOCMe$^+$	Tl/MeCOO/HClO$_4$/Me$_3$CC(O)Me = 1/3/2.2/1(H$_2$O)	2770	1163	–
Me$_3$CC(O)CH$_2$TlClNO$_3$	THF	2823	1078	–
Me$_3$CC(O)CH$_2$Tl(SSCNEt$_2$)$_2$	CHCl$_3$	2967	906	–
[MeC(O)]$_2$CHTlCl$^+$	Tl/Cl/HNO$_3$/MeC(O)CH$_2$C(O)Me = 1/1/2.2/1(H$_2$O)	2452	1380	–
MeC(O)CH$_2$C(O)CH$_2$TlCl$^+$	Tl/Cl/HNO$_3$/MeC(O)CH$_2$C(O)Me = 1/1/2.2/1(H$_2$O)	2693	1308	–
[MeC(O)]$_2$CHTlCN$^+$	Tl/CN/HClO$_4$/MeC(O)CH$_2$C(O)Me = 1/4/0.8/1(H$_2$O)	2568	1163	–
MeC(O)CH$_2$C(O)CH$_2$TlCN$^+$	Tl/CN/HClO$_4$/MeC(O)CH$_2$C(O)Me = 1/4/0.8/1(H$_2$O)	2774	1174	–
PhC(O)CH$_2$TlCl$^+$	Tl/Cl/HClO$_4$/PhC(O)Me = 0.5/0.5/1.1/0.5(S)	2805	1179	–
PhC(O)CH$_2$TlCl$_2$	THF	3227	1091	–
[PhC(O)CH$_2$]$_2$TlCl	THF/H$_2$O 3/2	2916	728	–
4′-ClPhC(O)CH$_2$TlCl$^+$	Tl/Cl/HClO$_4$/4′-ClPhC(O)Me = 0.5/0.5/1.1/0.5(S)	2806	1191	–
4′-MeOPhC(O)CH$_2$TlCl$^+$	Tl/Cl/HClO$_4$/4′-MeOPhC(O)Me = 0.5/0.5/1.1/0.5(S)	2774	1175	–
2′,4′,6′-Me$_3$PhC(O)CH$_2$TlCl$^+$	Tl/Cl/HClO$_4$/2′,4′,6′-Me$_3$PhC(O)Me = 0.5/0.5/1.1/0.5(S)	2845	979	–
2′-C$_{10}$H$_7$C(O)CH$_2$TlCl$^+$	Tl/Cl/HClO$_4$/2′-C$_{10}$H$_7$C(O)Me = 0.5/0.5/1.1/0.5(S) 2808	1182	–	

product appeared to be $[(CH_3)_3CC(O)CH_2Tl(OOCCH_3)]_2O$. All the three oxygen-bridged compounds give very broad ^{205}Tl NMR signals in the region expected for monoorganothallium(III) compounds. The elemental analyses of these compounds, their solubilities and IR spectra are not well reproducible, and detailed examination will be necessary for complete characterization of these interesting new materials.

The ^{205}Tl NMR parameters of the identified monoorganothallium(III) species are listed in Table 2. The chemical shifts of these species changed slightly as the reaction proceeded, and the chemical shifts shown are those recorded where the signals of the organothallium(III) species had just appeared, that is in the early stages of the reaction when the medium was still well defined.

Experimental

Materials

Aqueous solutions of $Tl(NO_3)_3$, $Tl(OOCCH_3)_3$ and $Tl(OOCCF_3)_3$ were prepared by dissolving commercial $Tl(NO_3)_3 \cdot 3H_2O$, $Tl(OOCCH_3)_3 \cdot 1\frac{1}{2}H_2O$ or $Tl(OCCCF_3)_3$, in a solution of the appropriate acid. Solutions of TlX_3 (X = Cl, Br) and $TlCl_2ClO_4$ were prepared by oxidation of a suspension of TlX or $TlClO_4$, by the relevant halogen until all the solid has dissolved; the excess of the halogen was removed by a stream of nitrogen. Solutions of $Tl(ClO_4)_3$ were made by anodic oxidation of $TlClO_4$ [35]. Solutions of $TlCl(ClO_4)_2$, $TlBr(ClO_4)_2$ and $TlCl(NO_3)_2$ were prepared by mixing an appropriate halogenide solution with a solution of $Tl(ClO_4)_3$ or $Tl(NO_3)_3$. Solutions of $Tl(CN)_n(ClO_4)_{3-n}$, ($n = 1$–3), were prepared by adding a solution of $Tl(ClO_4)_3$ to solid NaCN in a cooled vessel.

Analysis

Thallium(I) was determined by titration with 0.1 *M* solution of $KBrO_3$ with methyl orange as indicator. The total thallium content was obtained by reducing Tl^{III} with SO_2, boiling off the excess of SO_2, and titrating the solution against 0.1 *M* $KBrO_3$ [36]. The thallium content of the diethyldithiocarbamate complex was determined after oxidation with a solution of concentrated H_2SO_4 and H_2O_2 by boiling the mixture until it became colourless.

The chloride content was determined by the Volhard method after reduction of Tl^{III} to Tl^{I} with SO_2, removal of the excess of SO_2 by boiling, and cooling of the solution. Before back-titration with KSCN, nitrobenzene was added in order to protect the precipitated AgCl [37].

The acid concentration of Tl^{III} solutions was determined by titration against NaOH after addition of an excess of solid NaCl. In this way, the concentration of acid, Tl^{I}, and Tl^{III} could be determined one after the other in the same sample.

NMR measurements

The ^{205}Tl NMR spectra were normally recorded at 51.9 MHz and $27 \pm 0.5\,^\circ C$ on a Bruker MSL90 spectrometer. (The determination of the stability constant for reaction 2 was, however, performed at 230.8 MHz at $25 \pm 0.5\,^\circ C$ with a Bruker AM400 spectrometer.) The NMR parameters were chosen so that quantitative spectra could be obtained; typically, flip angle $\sim 30^\circ$ (2 μs), pulse repetition time 0.2 s, sweep width $\sim$ 80000 Hz, number of scans 1000. The chemical shifts are given in ppm with positive values at high frequency relative to an aqueous solution of

$TlClO_4$ extrapolated to infinite dilution. Peak integrals are accurate to ±10% and chemical shifts to about 0.2 ppm.

Preparations

(1) Preparation of $C_6H_5C(O)CH_2TlCl_2$. (a) Acetophenone (0.60 g, 5.0 mmol) was added to an acidified solution of $TlCl_2ClO_4$ (5.0 ml 1.00 *M* in $TlCl_2ClO_4$, and 0.20 *M* in $HClO_4$). The mixture was shaken from time to time during two days, and then crystallization of the product was initiated by scratching. The mixture was set aside for three days, and the solid then filtered off, washed with water (about 10 × 5 ml) until the filtrate no longer gave a white precipitate or opalescence on treatment with solid NaCl, dried in nitrogen stream, washed with ether (3 × 5 ml), and then dried again.

Yield: 1.46 g (74%). IR(Nujol): $\nu(C{=}O)$, 1620 cm^{-1}. Analysis. Found: Tl, 51.41; Cl, 17.81. $C_8H_7Cl_2OTl$ calcd.: Tl, 51.82; Cl, 17.98%.

(b) A solution of $HClO_4$ (0.15 ml of 6 *M*), concentrated HCl (0.73 ml), and acetophenone (0.53 g, 4.41 mmol), was added with stirring to a suspension of Tl_2O_3 (1.0 g, 2.19 mmol) in water (2.5 ml). Stirring was continued for two days, and crystallization of the product was initiated by scratching. The mixture was set aside until the solid was no longer sticky (about 4–6 days). The product was separated, washed and dried as described in (a).

Yield: 1.26 g (73%). Analysis. Found: Tl, 51.59; Cl, 17.85%.

Purification of partially decomposed $C_6H_5C(O)CH_2TlCl_2$. 1.0 g of the material was placed in a filter crucible (G3) and washed with THF (3 × 3 ml). The undissolved material was TlCl. The filtrate was evaporated in a nitrogen stream to leave a waxy residue, and ether (10 ml) was added, when crystallization was complete, the solid was filtered off, washed with ether (2 × 5 ml), and dried in a nitrogen stream. $C_6H_6C(O)CH_2Cl$ remains in the ethereal filtrate.

(2) Preparation of 4'-$(CH_3)C_6H_4C(O)CH_2TlCl_2$. The method used on the preparation and purification of $C_6H_5C(O)CH_2TlCl_2$ (method b) was employed but with 4'-methylacetophenone (0.59 g, 4.40 mmol) in place of acetophenone.

Yield: 0.90 g (50%). IR (Nujol): $\nu(C{=}O)$, 1609 cm^{-1}. Analysis. Found: Tl, 50.59; Cl, 17.53. $C_9H_9Cl_2OTl$ calcd.: Tl, 50.04; Cl, 17.36%.

(3) Preparation of 4'-$ClC_6H_4C(O)CH_2TlCl_2$. 4'-Chloroacetophenone (0.62 g, 4.0 mmol) was added to a mixture of acetonitrile (4.0 ml) and a solution of $TlCl_2ClO_4$ (4.0 ml, 1.00 *M* in $TlCl_2ClO_4$ and 2.18 *M* in $HClO_4$). The resulting homogeneous solution was kept at 24–25 °C for 25 h. Acetonitrile was then removed in a nitrogen stream, crystallization was initiated by scratching, and the mixture was set aside for 15–25 h. The product was filtered off, washed with water (8 × 4 ml), dried in N_2 stream, washed with ether (2 × 5 ml), and dried again.

Yield: 0.79 g (46%). IR (Nujol): $\nu(C{=}O)$, 1630, 1620(sh) cm^{-1}. Analysis. Found: Tl, 46.73; Cl bonded to Tl, 16.24. $C_8H_6Cl_3OTl$ calcd.: Tl, 47.65; Cl, 16.53%.

(4) Preparation of 2'-$C_{10}H_7C(O)CH_2TlCl_2$. 2'-Acetonaphthone (0.68 g, 4.0 mmol) was added to a mixture of acetonitrile (4.0 ml) and a solution of $TlCl_2ClO_4$ (4.0 ml, 1.00 *M* in $TlCl_2ClO_4$ and 2.18 *M* in $HClO_4$). The mixture was kept at ca. 25 °C for 17 h then the acetonitrile was removed in a nitrogen stream. The solid was filtered off, washed with water (5 × 4 ml), dried in N_2 stream, washed with ether (5 × 5 ml), and dried again. Yield: 0.49 g (28%). Analysis. Found: Tl, 45.14; Cl, 15.36. $C_{12}H_9Cl_2OTl$ calcd.: Tl, 45.98; Cl, 15.95%.

(5) Preparation of $CH_3C(O)CH_2TlClNO_3$. Acetone (1.0 ml, 13.6 mmol) was added to a solution of $TlCl(NO_3)_2$ (4.0 ml, 1.00 *M* in $TlCl(NO_3)_2$ and 2.2 *M* in HNO_3). After 1 h at ca. 25 °C the excess of acetone was removed in a nitrogen stream, and $NaHCO_3$ (about 1.07 g, 12.8 mmol) was added in portions until a pale yellow colour appeared. The solution was evaporated under vacuum at room temperature and the residual solid put into a filter crucible (G3) and extracted with THF (10 × 2 ml). The extract was kept at room temperature for 2 h, filtered into an ice-cooled vessel, and evaporated in a fast nitrogen stream. Ether (10–15 ml) was added to the residual thick oil, and the two phase system formed was stirred with a glass rod for 20 min, during which a solid formed. It was filtered off, washed with ether (3 × 2 ml) and dried in a nitrogen stream.

Yield: 0.69 g (48%). Analysis. Found: Tl, 56.18; Cl, 9.67. $C_3H_5ClNO_4Tl$ calcd.: Tl, 56.94; Cl, 9.88%.

Purification. The crude product (0.80 g) was dissolved in THF (16 ml) and the solution set aside for 30 min then filtered into a cooled vessel. The solid was separated from the filtrate in the way described for the crude product. Yield: 0.52 g (65%). Analysis. Tl, 56.88; Cl, 9.85%.

(6) Preparation of $(CH_3)_3CC(O)CH_2TlClNO_3$. 3,3-Dimethyl-2-butanone (0.60 ml, 4.80 mmol) was added to a mixture of acetonitrile (4.0 ml) and a solution of $TlCl(NO_3)_2$ (4.0 ml, 1.00 *M* in $TlCl(NO_3)_2$ and 2.2 *M* in HNO_3). The solution was kept at room temperature for 18 h, then solid $NaHCO_3$ (about 1.07 g, 12.8 mmol) was added in portions until the upper phase that formed during the neutralization had become pale yellow. The solution was evaporated at room temperature under vacuum, and the residual solid was extracted with THF (3 × 5 ml). The extract concentrated in a nitrogen stream to ca. 1 ml, then the product was precipitated by addition of ether (10–15 ml), filtered off, washed with ether (3 × 5 ml), and dried in a N_2 stream. The solid was redissolved in THF and again precipitated by addition of ether. Yield 0.83 g (52%). Analysis. Found: Tl, 50.83; Cl, 8.76. $C_6H_{11}ClNO_4Tl$ calcd.: Tl, 50.97; Cl, 8.84%.

(7) Preparation of $(CH_3)_3CC(O)CH_2Tl[S_2CN(C_2H_5)_2]_2$

3,3-Dimethyl-2-butanone (0.52 ml, 4.16 mmol) was added to a mixture of acetonitrile (4.0 ml) and an aqueous solution of $Tl(OOCCH_3)_3$ (4.0 ml, 1.00 *M* in $Tl(OOCCH_3)_3$ and 2.2 *M* in $HClO_4$). The mixture was kept at room temperature for 60 h then the acetonitrile was removed by bubbling N_2 through the solution. Solid $NaHCO_3$ (about 1.07 g, 12. 8 mmol) was added in portions until a pale yellow colour appeared. The solution was diluted with water (10 ml) and mixed with an aqueous solution (10 ml) of $NaS_2CN(C_2H_5)_2 \cdot 3H_2O$ (1.26 g, 5.60 mmol). The yellow oil that separated was extracted with $CHCl_3$ (5 × 6 ml), and the extract was dried with Na_2SO_4, filtered, evaporated in a nitrogen stream to 3 ml, and allowed to stand for 12–16 h at room temperature. The pale yellow solution was separated from the red crystalline material, mixed with ether (10 ml), and evaporated in a nitrogen stream. Ether (10 ml) was again added to the residue, and the solid was filtered off, dried, and extracted with THF (5 × 3 ml). The extract was set aside for 10–15 h then filtered and evaporated to dryness. Ether (10 ml) was added to the residue and the pale yellow product was filtered off then dried in N_2 stream. Yield 0.62 g (26%). IR (Nujol): ν(C=O), 1652 cm^{-1}. Analysis. Found: Tl, 35.16. $C_{16}H_{31}N_2OS_4Tl$ calcd.: Tl, 34.06%.

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