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FORMATION OF THALLIUM COMPLEXES WITH CARBON DIOXIDE DURING MASS SPECTROMETRY OF THALLIUM(I) CARBOXYLATES

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Summary

The effect of mass spectrometry on the behaviour of aryl-containing thallium(I) carboxylates of the $TlO_2CC_6H_4X$ type (where X denotes an aromatic ring substituent) has been studied. It has been shown that under electron impact, in the gas phase, $TlCO_2{}^+$ and $TlC_6H_4X^+$ ions tend to form, their ratio being governed by the nature and position of the substituent in the aromatic ring. A scheme of the fragmentation of thallium(I) carboxylates in the gas phase, where C_6H_4X and CO_2 fragments act as ligands, has been drawn up on the basis of the experimental data of 29 thallium compounds.

Earlier we showed that the fragmentation of alkyl-containing thallium(I) carboxylates under electron attack in the gas phase in mass spectrometry leads to selective formation of $TlCO_2{}^+$ ions. In the case of carboxylates of thallium with an aromatic radical or an unsaturated bond radical, only TlR^+ and $TlCO_2{}^+$ ions were formed during fragmentation under the same conditions [1]. We now report the results of a study of the influence of substituent X in the aromatic ring of the carboxylate ligand at Tl^I on the yield of the $TlCO_2{}^+$ adduct (cf. Table 1). It should be mentioned, that the fragmentation of $TlO_2CC_6H_4X$ carboxylates yields Tl^+, $TlCO_2{}^+$, $TlC_6H_4X^+$ and TlX^+ ions. Analysis of these data indicates that the process proceeds along two directions: (a) a C_6H_4X fragment breaks off, forming the $TlCO_2{}^+$ ion; (b) the TlR^+ ion is formed due to decarboxylation of the molecular ion. The complete fragmentation is shown in Scheme 1, where X denotes aromatic ring substituent.

Scheme 1 shows that during the fragmentation of alkyl-containing thallium(I) carboxylates, the process proceeds along the first direction, while if R is an aryl or unsaturated radical, the fragmentation of these carboxylates proceeds along both directions (overall contribution to the fragmentation scheme is determined by the contributions of the individual carboxylates). Thus, as in the case of thallium

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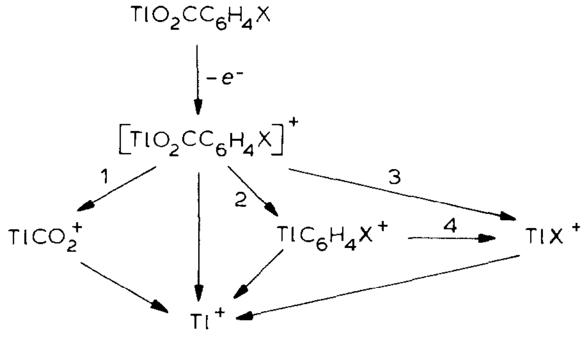
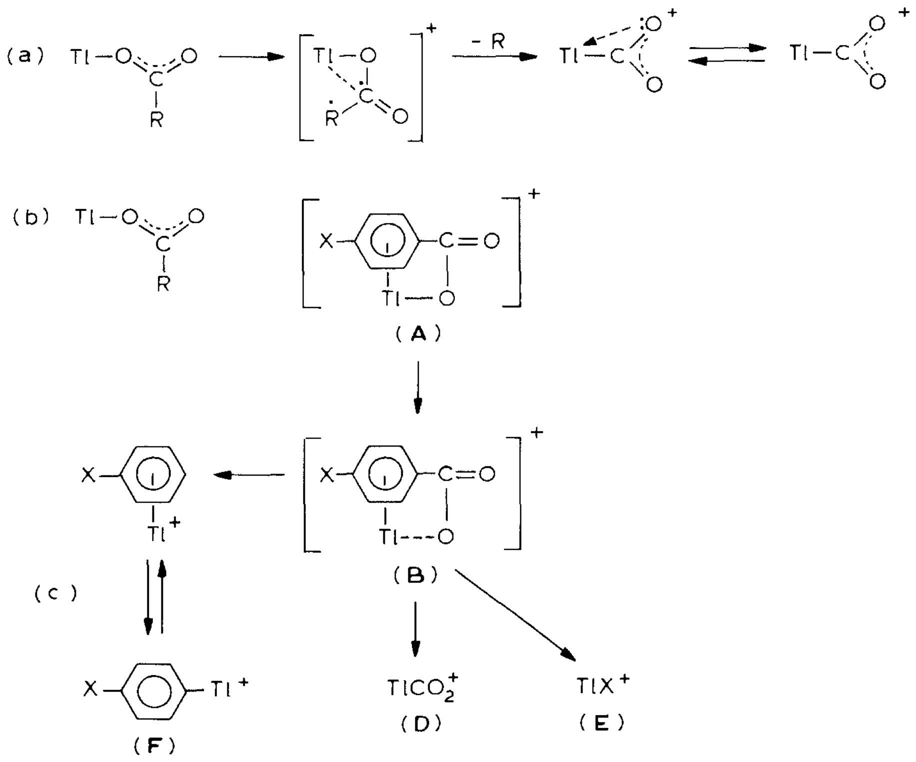
SCHEME 1



benzoate, the $TlCO_2{}^+$ ion contribution to the fragmentation scheme amounted to 15.76%; for the Tl^+ ion it was 35.95% (Table 1). In order to elucidate the behaviour of thallium(I) carboxylates in the gas phase under electron impact, and to point out the difference in the process of their fragmentation in the cases where R = alkyl and aryl, a detailed scheme of the fragmentation mechanism relevant to both cases was drawn up (Scheme 2).

Scheme 2 shows that both cases imply the formation of a metal–carbon bond for the $TlCO_2{}^+$ and $TlC_6H_5{}^+$ ions. Rather stable univalent thallium compounds with

SCHEME 2



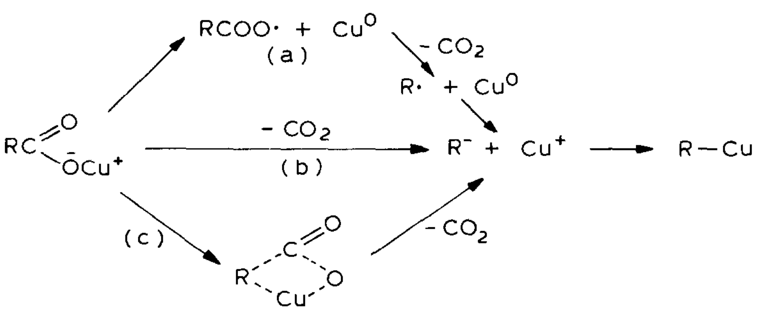
σ-aryl and π-cyclopentadienyl rings have been described in the literature [2–4]. It is significant that the metal–carbon bond in the π-complex CpTl is much shorter (by 0.4 Å) than the sum of the atomic radii [4–6], which, according to Tyler et al. [6] is due to metallotropic transformation with the formation of a metal–carbon σ-bond. It is feasible that such a transformation takes place for thallium with a phenyl ring, which leads to a stable molecular ion in stages (**A**) and (**B**), and further interaction of the thallium atom with each carboxylate ligand fragment.

It is interesting that, according to some Swedish authors [7–9], the decarboxylation of aryl-containing copper carboxylates during thermolysis proceeds along similar lines (cf. Scheme 3).

On the basis of these experimental data, the π-complex is formed as an intermediate between the aromatic ring and the Cu^+ ion during decarboxylation of aryl-containing carboxylates of copper. The C-anion, which is formed in the next stage, is stabilized by conjugation with this π-bond. As a result, the copper ion has time to migrate from the π-bond with formation of σ-arylcopper (route b, Scheme 3). It is necessary to note the formation of the intermediate along direction c (Scheme 3). On the basis of our calculations and experimental mass spectrometric data of thallium(I) and copper(I), copper(II) carboxylates, it should be stated that an analogous intermediate can form during fragmentation of these carboxylates under electron impact (cf. [1,10] and references cited therein). As can be seen from Scheme 3, this intermediate can generate both MCO_2 and MR adducts.

According to our calculations, and experimental mass spectrometric data of thallium(I) carboxylates, the CO_2 molecule competes successfully for the coordination site near the thallium atom with aromatic and unsaturated radicals [10]; this was not observed for copper. From our point of view, this is possible because of the existence of a three-centred cycle between the CO_2 molecule and the metal atom. In this case, the carbon atom acts as an acceptor, while the oxygen atom acts as a donor of electron density (π-type coordination). It should be emphasized that such coordination has been observed and confirmed by X-ray structure analysis for the carbon dioxide nickel complex. In a previous paper [1], we pointed out that the actual Tl–C bond in the $TlCO_2$ adduct is 0.5 Å shorter than the sum of the atomic radii. It is probably this circumstance that enables the CO_2 molecue to compete successfully with the aromatic or unsaturated ligand for the coordination site near the thallium atom. Table 1 shows the contribution of the $TlCO_2{}^+$ ion to the thallium acrylate fragmentation scheme to be an order of magnitude higher than that of the

SCHEME 3



TlR^+ ion, whereas during thallium cinnamate fragmentation it is the contribution of the $TlCH{=}CHC_6H_5^+$ ion that is higher than the contribution of $TlCH{=}CH_2^+$, and the $TlCO_2^+/TlCH{=}CHC_6H_5^+$ ratio is close to the $TlCO_2^+/TlC_6H_5^+$ ratio in the case of thallium benzoate. It is obvious that this is due to aromatic ligand participation in the coordination with Tl atoms.

We believe that the mass spectrometric data of thallium perfluorobenzoate are also of interest: TlR^+ ion was absent from the mass spectrum. The only ion found in the gas phase was $TlCO_2^+$. This is explained by the fact that the electron-poor fluorinated ring is incapable of forming a π-bond with the thallium atom; fragmentation therefore proceeds along the first direction. This is partly confirmed by the absence of a molecular ion in the gas phase.

A number of thallium(I) carboxylates of the $TlO_2CC_6H_4X$ type (where X denotes the aromatic ring substituent) were investigated. It should be mentioned that a certain influence on $TlCO_2^+$ and TlR^+ ion formation in the gas phase during electron impact was brought about by various substituents and their positions in the ring. In particular, during the transition from electron-accepting to electron-donat-

TABLE 1

INFLUENCE OF THE CARBOXYL LIGAND SUBSTITUENT ON THE FRAGMENTATION OF THALLIUM(I) CARBOXYLATES DURING MASS SPECTROMETRY

No.	Thallium carboxylate	$TlCO_2^+$	TlR^+	$TlCO_2^+/TlR^+$	M^+	Tl^+
1	$CHCO_2Tl$	13.5	–	–	–	86.50
2	CH_3CO_2Tl	10.5	–	–	–	89.47
3	$C_2H_5CO_2Tl$	2.05	–	–	–	97.9
4	CH_2CHCO_2Tl	10.75	1.06	10.14	–	88.18
5	$C_6H_5CO_2Tl$	15.76	35.95	0.43	7.8	40.42
6	$C_6F_5CO_2Tl$	1.18	–	–	–	98.80
7	$C_6H_5CH{=}CHCO_2Tl$	2.57	7.46	0.34	4 28	85.68
8	$p\text{-}NO_2C_6H_4CO_2Tl$	17.5	5.42	3 22	0.61	76.45
9	$m\text{-}NO_2C_6H_4CO_2Tl$	4.6	19.1	0.24	–	76.33
10	$o\text{-}NO_2C_6H_4CO_2Tl$	–	6.27	–	–	93.72
11	$p\text{-}OCH_3C_6H_4CO_2Tl$	1.78	5 82	0.32	5.48	86.92
12	$m\text{-}OCH_3C_6H_4CO_2Tl$	5.02	9.96	0.50	10.01	74.90
13	$o\text{-}OCH_3C_6H_4CO_2Tl$	4.81	4.19	1.14	3.49	87 48
14	$p\text{-}NH_2C_6H_4CO_2Tl$	1.71	11.9	0.14	31.37	55.03
15	$m\text{-}NH_2C_6H_4CO_2Tl$	3.42	14.87	0.22	18.31	63.37
16	$o\text{-}NH_2C_6H_4CO_2Tl$	1.88	12.31	0.15	3.77	82 10
17	$p\text{-}CH_3C_6H_4CO_2Tl$	3.12	11 65	0.26	0.76	84.46
18	$m\text{-}CH_3C_6H_4CO_2Tl$	6.25	12.5	0.50	4.95	76.27
19	$p\text{-}FC_6H_4CO_2Tl$	15.45	13.79	1.12	11.29	59.45
20	$m\text{-}FC_6H_4CO_2Tl$	10.31	6.90	1.49	3.41	79.36
21	$p\text{-}ClC_6H_4CO_2Tl$	14.19	9.58	1.48	5.25	70.97
22	$m\text{-}ClC_6H_4CO_2Tl$	6.45	6.45	1.0	6.45	80.64
23	$o\text{-}ClC_6H_4CO_2Tl$	3.19	19.10	0.16	3.34	74.34
24	$p\text{-}BrC_6H_4CO_2Tl$	10.48	4.64	2.25	4.80	80.06
25	$m\text{-}BrC_6H_4CO_2Tl$	9.80	5.88	1.67	5.88	78.43
26	$o\text{-}BrC_6H_4CO_2Tl$	0.93	5.78	0.16	0.10	88.50
27	$p\text{-}IC_6H_4CO_2Tl$	0.80	5.71	0.14	6.84	80.50
28	$m\text{-}IC_6H_4CO_2Tl$	11.50	7.49	1.53	7.62	68.00
29	$o\text{-}IC_6H_4CO_2Tl$	9.85	7.82	1.25	7.96	68.70

ing substituents, the $TlCO_2^+$ ion contribution was expected to decrease, while that of TlR^+ was expected to increase in the fragmentation scheme. In fact, as seen from Table 1, the introduction of such a strong electron-accepting substituent as a nitro group into the *para* position of the ring invariably leads to an increase of the $TlCO_2^+$ ion contribution to a total value of 17.5%. The introduction of strong electron-donating substituents into the *para* position, such as OCH_3, CH_3, NH_2, decreases the $TlCO_2^+$ ion contribution notably to 1.78, 3.12 and 1.71%, respectively, while the TlR^+ contribution increases. Substituents such as halogens occupy the middle position between electron-accepting and electron-donating substituents, according to their capacity to draw electron density away from the ring. Therefore the introduction into the *para* position of the ring of such substituents as Cl, F, Br and I leads to comparable contributions of the $TlCO_2^+$ and TlR^+ ions to the fragmentation scheme.

Introducing the substituent into the *meta* position of the ring shifts the fragmentation process somewhat towards direction 2 (Scheme 1) with an electron-accepting substituent, and towards direction 1 with an electron-donating substituent. The formation of either ion appears to be governed not only by the stability of the newly formed compounds, but also by the ease with which the initial C–C bond can be broken when the radical is separated from the carboxylate group, which naturally is connected with the position of the substituent in the aromatic ring.

It should be mentioned that during the fragmentation of *ortho*-substituted carboxylates, a decrease or, as was the case with *ortho*-$NO_2C_6H_4CO_2Tl$, the total absence of $TlCO_2^+$ ion in the gas phase was recorded. This, in our opinion, is explained by the "*ortho*-effect", i.e. intramolecular interaction of substituents with a nearby thallium atom. Thus, during the fragmentation of *ortho*-BrC_6H_4COOTl, a peak was recorded in the mass spectrum corresponding to the $TlBr^+$ ion with a 5.2% intensity of 5.7% was recorded. Scheme 2 shows that TlX^+ (**E**) may be formed either along direction 3 or along 4, i.e. the thallium atom may interact directly with the aromatic ring substituent. This is confirmed by the formation of the $TlBr^+$ ion in a 1.8% yield in the case of fragmentation of *m*-$BrC_6H_4CO_2Tl$ (TlI^+, 7.1% for *p*-$IC_6H_4CO_2Tl$ and TlI^+, 5.5% for *m*-$IC_6H_4CO_2Tl$).
p-$IC_6H_4CO_2Tl$ and TlI^+, 5.5% for *m*-$IC_6H_4CO_2Tl$).

On the basis of the experimentally obtained data, we conclude that during fragmentation of univalent thallium carboxylates under electron impact, formation of the $TlCO_2^+$ ion is possible in the gas phase when R is an alkyl group. When R is an aryl or unsaturated radical, the CO_2 molecule successfully competes for the coordination site near the metal atom with the aromatic ring, which is in total accordance with a stability calculation for a number of structures with a thallium adduct and CO_2 described in ref. 10.

Experimental

The production of univalent thallium carboxylates studied in the present paper has been described in a previous paper [12]. Mass spectra were obtained on an MS-30 apparatus with a DS-50 recorder. The temperatures of direct probe introduction were 200–350 °C, ionization chamber temperature was 300 °C, and ionizing voltages were 12 and 70 eV.

References

1 Yu.S. Nekrasov, S.Yu. Silvestrova, T.V. Lysiak, Z.M. Alaudinova, Yu Ya Kharitonov and I.S. Kolomnikov, Koord. Khim., 7 (1981) 1270.
2 H. Gilman and R.G. Jones, J. Am. Chem. Soc., 62 (1940) 2357.
3 L.T. Reynolds and G.J. Wilkinson, J. Inorg. Nucl. Chem., 5 (1959) 86.
4 E. Frasson, F. Menegue and C. Panattoni, Nature (London), 199 (1963) 1087.
5 S. Shibata, L.S Bartell and R.M. Gavin, J. Chem. Phys., 41 (1964) 717.
6 J.K. Tyler, A.P. Cox and J. Sheridan, Nature (London), 183 (1959) 1182.
7 T. Cohen and R.A. Schanbach, J. Am. Chem. Soc., 92 (1970) 3189.
8 M. Nilsson, Acta Chem. Scand., 20 (1966) 423.
9 C. Björklund and M. Nilsson, Acta Chem. Scand., 22 (1968) 2585.
10 Yu.A. Borisov, Yu.S. Nekrasov, T.V. Lysyak, I.S. Kolomnikov and Yu.Ya Kharitonov, Koord. Khim., 4 (1978) 1512.
11 M. Aresta, C.F. Nobile, V.G. Albano, E. Forni and M. Manassero, Chem. Commun., 15 (1975) 636.
12 T.V. Lysyak, S.L. Rusakov, I.S. Kolomnikov and Yu.Ya. Kharitonov, Z. Neorg. Khim., 28 (1983) 1339.