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COMPLEXES OF CARBON DIOXIDE WITH COPPER AND THALLIUM AS ORGANOMETALLIC COMPOUNDS: MASS SPECTROMETRIC INVESTIGATION AND CALCULATION

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Summary

It has been shown that under electron impact the carboxylates of thallium and copper in the gaseous phase produce the adducts $TlCO_2^+$ and $CuCO_2^+$, respectively. Mass spectrometric data in combination with calculations by the virial statistic method indicate the existence of a metal–carbon bond in the MCO_2^+ adducts.

In recent years, interest in complexes of carbon dioxide with transition metals has grown considerably, and the possibility of such complexes existing in the form of stable adducts has been shown [1–3]. In a number of processes the formation of unstable complexes of CO_2 with transition metals is observed (or, at least, is supposed to take place) [1]. In particular, Eder's reaction is supposed to proceed with intermediate formation of the $CuCO_2$ adduct [3–5]. The formation of similar copper complexes is also likely to take place in different decarboxylation reactions catalysed with copper salts [6–8].

MCO_2^+ ions were also observed in the mass spectra of copper and thallium carboxylates [9–14]. Yet, the problems of the structure and stability of these ions have not been discussed anywhere. This problem, however, is of principal importance in understanding the mechanisms of various reactions proceeding with the participation of CO_2 [1,2], including the reactions of fragmentation of metal carboxylates, which proceed in the gaseous phase under electron impact [9–14].

In the present paper we report our mass spectrometric investigation of carboxylates of mono- and di-valent copper and of mono- and tri-valent thallium. The spectral data of the latter compounds are given in Table 1. Overall, our results for copper carboxylates are in agreement with the data reported by other authors [9–13].

The spectra of the Cu^I and Cu^{II} derivatives are similar, except for the $CuOOCR^+$

TABLE 1

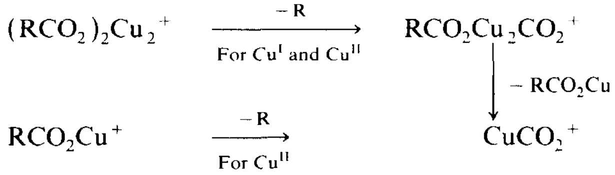
RELATIVE INTENSITIES OF THE SAME FRAGMENT IONS IN THE MASS SPECTRA OF THALLIUM CARBOXYLATES [a]

Ion	$TlOOCCH_3$	$TlOOCC_6H_5$	$(CH_3)_2TlOOCCH_3$	$(CH_3)_2TlOOCC_6H_5$
P^+		4		
$[P-CH_3]^+$			10	11
$[TlC_6H_5]^+$		11		2.7
$[TlCO_2]^+$	7	5	30	2
$[Tl(CH_3)_2]^+$			31	34
Tl^+	100	100	100	100

[a] The values of the relative intensities for ^{205}Tl are given.

ions which are present only in the mass spectra of the carboxylates of divalent copper (R = H, CH_3, n-C_3H_7, i-C_3H_7).

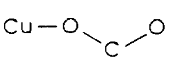
The $CuCO_2{}^+$ ion present in the mass spectra of the carboxylates of mono- and di-valent copper is probably formed from the $(RCO_2)_2Cu_2{}^+$ ion as a result of successive or simultaneous loss of R and CuO_2CR:

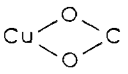


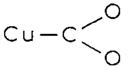
In the case of carboxylates of divalent copper, the formation of the $CuCO_2{}^+$ ion may also proceed from the CuO_2CR^+ ion through elimination of the R radical.

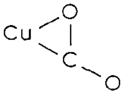
It should be noted that the stability of the $CuCO_2{}^+$ ion is relatively high; its intensity, depending on the nature of the radical, ranges from 1 to 7% for Cu^I and from 1.5 to 17% for Cu^{II} [11,13].

In principle, $CuCO_2{}^+$-type ions, with regard to the bending of carbon dioxide in complex formation with a metal [1], may have structures of the following types:

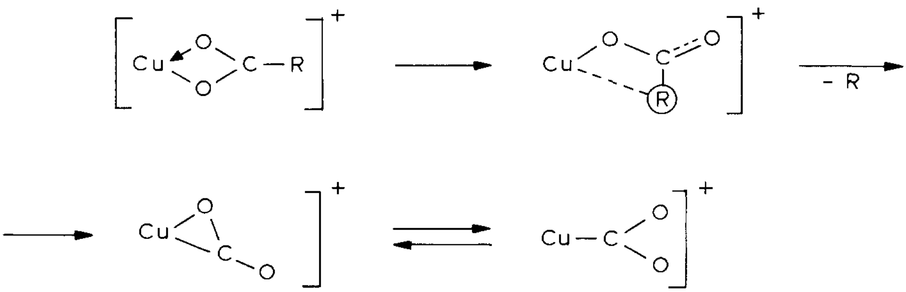

(I)


(II)


(III)


(IV)

According to the data calculated by the virial statistic method [15], these structures, in terms of their stability, make up the following sequence: IV > III ≫ ≫ I ≫ II [16]. Therewith, while the complexation of the CO_2 molecule with a copper ion according to type IV amounts to ca. 36 kcal/mol, the complexation according to type II is a process energetically unfavourable altogether (the energy loss being 60 kcal/mol). X-Ray analysis data show the coordination of carbon dioxide in the complex $[(C_6H_{11})_3P]_2Ni \cdot CO_2$ to be according to type IV [17]. On the whole, the process of decarboxylation of copper carboxylates as a result of electron impact may be represented by the following scheme:



As a result of splitting the C–C bond of the carboxylate fragment at the metal centre, both organometallic compounds of the M–R type and complexes of copper with CO_2 may be formed.

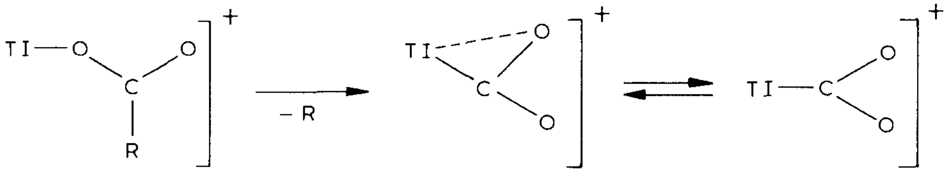
Fragmentation of copper carboxylates of saturated acids turned out to be present in the elimination of the radical R with the formation of $Cu_2(O_2CR)CO_2{}^+$ ions, and the fragmentation of copper carboxylates of unsaturated and aromatic acids to be characterized by the elimination of CO_2 with the formation of the $Cu_2(O_2CR)R^+$ ion [9–14].

The second pathway is probably conditioned by the formation of stable organometallic compounds of copper with olefins and arenes [12,13]. The absence, in this case, of fragments in which CO_2 occurs in the form of a ligand indicates that carbon dioxide is incapable of competing for the coordination site of the copper atom with olefins or aromatic ligands. Thus, in the whole series of copper carboxylates of aromatic and unsaturated acids a low-intensity peak of $CuCO_2{}^+$ is observed only for copper acrylate and copper vinyl acetate [13].

In copper carboxylates of unsaturated acids, fragmentation with the formation of intensive peaks of $CuCO_2{}^+$ ions takes place. According to calculations, the stabilization of these ions, in all likelihood, is conditioned by the participation in the coordination with the metal, of both the oxygen atom and the carbon atom of the CO_2 molecule (type IV).

The $TlCO_2{}^+$ ions present in the mass spectra of carboxylates of mono- and tri-valent thallium, in contrast to copper complexes, are formed in the fragmentation of both saturated and aromatic acids (Table 1). These results are indicative of a higher stability of $TlCO_2{}^+$ compared with $CuCO_2{}^+$. From the analysis of the X-ray data for the carboxylates and organometallic complexes of copper and thallium, which was carried out with a view to selecting reasonable parameters (bond length, angle) for calculations [16], it follows that such a difference is conditioned by the greater strength of the Tl–C σ-bond (shortening of this bond in the molecules reaches the value of 0.5 Å compared to the sum of the atomic radii, whereas in the case of copper such a difference is practically absent). Moreover, according to the calculated data for $TlCO_2{}^+$, structures III and IV hardly differ in energy, which can be explained by the considerable difference in the observed lengths of the Tl–O and

Tl–C bonds in the carboxylates (while the Cu–O and Cu–C distances are similar). Proceeding from the above and taking into account the monodentate nature of Tl^{1} carboxylates, we can suppose that their fragmentation may proceed via the distorted π-complex IV:



(I) (IV) (III)

It is of interest that in the stable organometallic compound of mercury $\mathrm{ClHgCOOCH_3}$, according to the structural data, the ligand $\mathrm{COOCH_3}$ is monodentate (type III) [18]. For the same compound it is characteristic that the length of the Hg–C σ-bond (1.96 Å) is much shorter than the lengths of the Hg–C σ-bonds (2.07 to 2.10 Å) in $\mathrm{R_2Hg}$-type compounds (R = H, $\mathrm{CH_3}$, $\mathrm{C_6H_5}$) [16].

Thus, mass spectrometric data in combination with virial statistic calculations [16] indicates the existence of stable organometallic complexes of copper and thallium with $\mathrm{CO_2}$.

References

1 I.S. Kolomnikov and M.Ch. Grigorjan, Usp. Khim., 4 (1978) 6603.
2 I.V. Stankevich, T.V. Lysyak, G.G. Aleksandrov and I.S. Kolomnikov, Zh. Struct Khim., 5 (1978) 908.
3 M.E. Volpin and I.S. Kolomnikov, Organometallic Reactions, 5 (1975) 313.
4 S.J. Adler and R.M. Noyes, J. Am. Chem. Soc., 77 (1965) 2036.
5 T.L. Allen, J. Am. Chem. Soc., 73 (1951) 3589
6 A. Cairncross, J.R Rolands, R.M. Heuklorson and W.A. Sheppard, J. Am. Chem Soc, 91 (1970) 3187.
7 T. Cohen and R. Schambach, J. Am Chem. Soc., 92 (1970) 3189.
8 J. Chrochoweka-Palicka and M. Nilsson, Acta Chem. Scand., 25 (1971) 3451.
9 C.R Reichert, D.K.C. Fung, D.C.K. Lin and J.B. Westmore, Chem. Commun., (1968) 1094.
10 Ch.Sh. Khariton, A.B. Ablov and G.A. Popovitch, Dokl. Akad. Nauk SSSR, 204 (1972) 1374.
11 D.A. Edwards and R. Richards, Inorg. Nucl. Chem. Letters, 8 (1972) 783.
12 D.A. Edwards and R. Richards, J. Chem. Soc., Dalton, (1973) 2463.
13 T. Ogura and Q. Fernando, Inorg. Chem., 12 (1973) 2611.
14 A.T. Hsieh, A.G. Lee and P.L. Sears, J. Org. Chem., 37 (1972) 2637.
15 Yu.A. Borisov, Zh. Struct. Khim., 17 (1976) 974, 979.
16 Yu.A. Borisov, T.V. Lysyak, Yu.S. Nekrasov, Yu.Ya. Kharitonov and I.S. Kolomnikov, Koord. Khim., 4 (1978) 1318
17 M. Aresta, C.F. Nobile, V G. Albano, E. Forni and M. Monassero, Chem Commun, (1975) 636.
18 T.C. Mack and J. Trotter, J. Chem. Soc., (1962) 3243.