CARBOXYL GROUP -CO_2 EXCHANGE IN THE THERMAL DECOMPOSITION OF ALIPHATIC DICARBOXYLIC ACID SALTS.

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SUMMARY

The exchange reaction of carboxyl groups with carbon dioxide has been studied in thermal decomposition of aliphatic dicarboxylic acid disodium salts. It has been found that exchange takes place under given experimental conditions. In some cases the process results in considerable exchange even in lower conversion ranges therefore it is of significance in the field of isotopes techniques.

INTRODUCTION

As known(1-4), the exchange of carboxyl groups in the thermal transformation of aliphatic carboxylate salts can be detected by isotope techniques (Fig.1). The rate of this exchange is known(5) to depend on the nature of corresponding cation. If the exchange process shows some analogy to the Henkel reaction then on the basis of a widely accepted mechanism for such transformations(6-9) (Fig.2), exchange between carboxyl groups and CO_2 can be expected too. These findings seem to justify the study of this phenomenon in the case of aliphatic carboxylate salts in spite of the observation of Bühler and coworkers(10) who stated that the thermal decomposition process of lithium phenylacetate effected in the presence of $^{14}CO_2$ was accompanied only with a slight incorporation of ^{14}C into the residual phenylacetic acid.

$$\begin{array}{lcl} R\text{-}^{14}COOM & & R\text{-}COOM \\ & \rightleftharpoons & \\ R'\text{-}COOM & & R'\text{-}^{14}COOM \end{array}$$

Fig.1

In this paper we wish to report our experimental results obtained for the exchange reactions of carboxyl groups with $^{14}CO_2$ studied in the thermal transformation process of some aliphatic dicarboxylic acid disodium salts.

$$C_mH_n\text{-}COOM \longrightarrow (C_mH_n)^- + M^+ + CO_2$$

$$C_mH_n\text{-}COOM + (C_mH_n)^- \longrightarrow C_mH_{n+1} + (C_mH_{n-1}\text{-}COOM)^-$$

$$(C_mH_{n-1}\text{-}COOM)^- + CO_2 + M^+ \rightleftharpoons C_mH_{n-1}\,(COOM)_2$$

Fig.2

EXPERIMENTAL

Starting materials

Preparation of sodium salts was carried out by the following method. An equivalent amount of NaOH solution was added to carboxylic acid in water. The solution was evaporated and dried *in vacuo* at 200 °C for 2 hours. Purity of the product was checked by Na analysis.

Ethane-1,1,2-tricarboxylic acid

The compound was prepared from ethyl α-bromoacetate and diethylmalonate by the method used for pentane-1,1,5-tricarboxylic acid. The ester formed was distilled *in vacuo* (b.p. 155 °C/8 mm Hg). The tricarboxylic acid obtained in the course of alkaline hydrolysis was crystallized from water; m.p. 158-9 °C; yield 52 % (for ethyl α-bromoacetate).

Propane-1,1,3-tricarboxylic acid

The triethyl ester (b.p. 155 °C/6 mm Hg) was prepared as described above from diethyl malonate and β-bromopropionic acid ethyl ester than subjected to alkaline hydrolisis. The acidified reaction mixture was evaporated to dryness and the tricarboxylic acid dissolved with alcohol from the solid residue. The alcohol was distilled and, on the addition of acetone, the syrupy residue crystallized. Yield 55 % (for ethyl β-bromopropionate); m.p. 140-42 °C.

Butane-1,1,4-tricarboxylic acid

The triethyl ester of this acid (b.p. 175 °C/12 mm Hg) was prepared and then hydrolyzed by the method mentioned above. The butanetricarboxylic acid was precipitated from concentrated ethyl acetate solution with petroleum ether. Yield 61 % (based on ethyl γ-bromobutyrate); m.p. 139-40 °C.

Pentane-1,1,5-tricarboxylic acid

Ethyl δ-bromovalerate was reacted with diethyl malonate in the presence of sodium ethoxide. The resulting triethyl ester was distilled in vacuo (b.p. 165-70 °C/4 mm Hg) and hydrolyzed in aqueous solution of KOH(11). The homogenous solution was concentrated then acidified with cc. HCl to pH 1 and extracted with ether. The extract was dried over Na_2SO_4 and evaporated to dryness. Yield 62 % (based on ethyl δ-bromovalerate); m.p. 39-90 °C (from ether — petroleum ether).

Method for the study of the exchange reaction

The study of thermostability and the choice of reaction conditions were effected on the basis of derivatograms recorded by a MOM type Erdey-Paulik derivatograph in N_2 stream (15 l/hr). The results are shown in Table I.

The exchange reaction carried out in a metal bath thermostat was studied in the following way.

On placing dicarboxylic acid disodium salt (10 mM) in a tube and distilling $^{14}CO_2$ (2 mM; spec.act. 1.88-10^7 dpm/mM) the tube was sealed and placed in a thermostat and kept at an appropriate temperature. In elaborating the samples, the conversion was determined by the isotope dilution method from an aliquot of the aqueous salt solution. The recovered acids were purified by repeated recrystallizations. Purity of the products was checked by m.p. and C, H analysis. Radioactivity measurements were performed in dioxane solution by means of a Packard Tri-Carb scintillation spectrometer Model 574. The results are given in Table II.

Table I
Thermogravimetric parameters of the sodium carboxylates

Salts*	Decomposition temperature (°C)		Weight loss (%) in the stage	
	Initial	DTG peak	1	2
MNa	320	350, 510	12	13
MMNa	370	400, 500	18	9
EMNa	370	430, 510	22	10
SNa	420	430 –	33	–
ETNa	330	390, 470	10	10
GNa	450	500 –	38	–
PRTNa	350	380, 480	8	14
ANa	440	480 –	41	–
BTNa	400	460 –	32	–
PNa	410	500 –	44	–
PTNa	380	430, 500	8	28

* Abbreviations:
MNa: Disodium malonate; MMNa: Disodium methylmalonate; EMNa: Disodium ethylmalonate; SNa: Disodium succinate; ETNa: Ethane-1,1,2-tricarboxylic acid trisodium salt; GNa: Disodium glutarate; PRTNa: Propane-1,1,3-tricarboxylic acid trisodium salt; ANa: Disodium adipate; BTNa: Butane-1,1,4-tricarboxylic acid trisodium salt; PNa: Disodium pimelate; PTNa: Pentane-1,1,5-tricarboxylic acid trisodium salt.

Table II

Exchange data

Salts*	Temperature (°C)	Time (min)	Conversion (%)	Radioactivity of residue acid (10^6 dpm/mM)	Exchange** (%)
MNa	330	60	53	0.728	21.3
MMNa	360	120	72	1.250	36.6
EMNa	380	120	67	0.964	28.2
SNa	440	30	47	2.620	76.6
GNa	420	60	15	0.191	5.6
ANa	420	60	0	0	0
ANa	440	60	72	0.711	20.8
ANa	450	60	85	0.800	23.4
PNa	390	60	0	0	0
PNa	410	120	40	0.643	18.8
PNa	420	120	59	1.380	40.4

* Abbreviations are the same as in Table I.

** These particulars give the extent of equilibrium distribution in percentage.

EXPERIMENTAL RESULTS AND DISCUSSION

According to Table II, considerable exchange can be observed between the carboxyl groups and CO_2 in the thermal decomposition of the salts. This exchange reaction is in some instances so fast that it nearly leads to equilibrium distribution even in lower ranges of conversion, therefore it is of considerable importance in the field of isotope tracer techniques(12).

The remarkable difference in the thermal transformation processes of aromatic and aliphatic carboxylic acid salts may probably be attributed to the presence and great mobility of α-hydrogens(13). Consequently, in the course of the thermal decomposition of aliphatic carboxylic salts, hydrogen splitting and subsequent carboxylation will mainly occur on the α-carbon atom resulting malonate type intermediates (Fig.3).

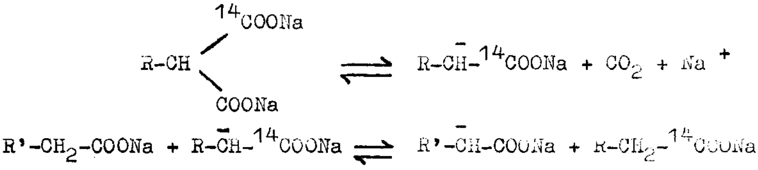
$$R\text{-}CH_2COOM \longrightarrow (R\text{-}CH_2^-) + CO_2 + M^+$$

$$R\text{-}CH_2COOM + R\text{-}CH_2^-) \longrightarrow R\text{-}CH_3 + (R\text{-}\overset{-}{C}H\text{-}COOM)$$

$$(R\text{-}\overset{-}{C}H\text{-}COOM) + CO_2 + M^+ \rightleftharpoons R\text{-}CH(COOM)_2$$

Fig.3

The latter have, however, shown no thermostability under the experimental conditions chosen (Table I), and after decarboxylation and subsequent hydrogen splitting these are transformed into the starting salts, producing another proton deficient fragment. Thus, in addition to the hydrogen transfer process$^{(14,15)}$, decarboxylation of the malonate type product formed in carboxylation also takes part in this fragment-reproducing process (Fig.4).



$$R\text{-}CH(^{14}COONa)(COONa) \rightleftharpoons R\text{-}\overset{-}{C}H\text{-}^{14}COONa + CO_2 + Na^+$$

$$R'\text{-}CH_2\text{-}COONa + R\text{-}\overset{-}{C}H\text{-}^{14}COONa \rightleftharpoons R'\text{-}\overset{-}{C}H\text{-}COONa + R\text{-}CH_2\text{-}^{14}COONa$$

Fig.4

It is in the latter reaction that the exchange between carboxyl groups and CO_2 occurs in our interpretation of the mechanism.

In our opinion, it is highly probable that the proton deficient fragment in α-position plays a decisive role in the exchange reactions. The individual stabilization and formation processes of these fragments constitute the dynamic state of the substance, which, under given experimental condiditons, gives the above fragments' a macroscopic existence on the one hand, and, on the other, brings about the above outlined detectable changes.

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