

THERMAL TRANSCARBOXYLATION REACTIONS. II*. THE STUDY OF CARBOXYL GROUP EXCHANGE IN THE COURSE OF KETONE FORMATION

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SUMMARY

The course of carboxyl group exchange in the thermal decomposition of a mixture of disodium adipate and pimelate has been studied using ^{14}C -labelled compounds. The exchange data obtained from the residual acids and ketone formed point to two different incorporation processes. This phenomenon can be well interpreted by presuming the presence of a malonate type intermediate formed in the decomposition process.

Bühler and coworkers¹ reported that an exchange of ^{14}C -labelled and unlabelled carboxyl groups (Fig.1) can be observed in the ketonic pyrolysis of aliphatic alkali carboxylates. The exchange is well detectable in the residual acid and in the ketone formed as well. This finding was also confirmed by other authors,²⁻⁴ but little is known about the details of the reaction

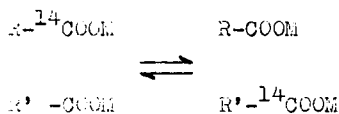


Fig.1

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The mechanism of ketonic pyrolysis was interpreted by Bunker² as shown in Fig.2. According to this mechanism the exchange reaction takes place prior to ketone formation,

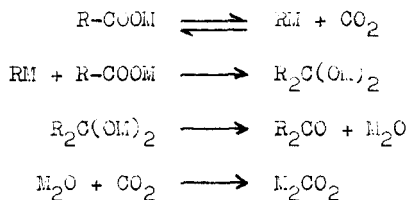


Fig.2

as ^{14}C -labelled ketone can be derived only from ^{14}C -labelled salt. In other words, if the above mechanism is true the change in radioactivity of the residual acid is equal to, or exceeds, the value found in the ketone formed. We studied this question in the thermal decomposition of a mixture of sodium adipate and pimelate with one of the components labelled with ^{14}C in the carboxyl group. The exchange was measured simultaneously in the residual acids and ketones formed.

Optimal conditions for the reaction were determined with thermo-gravimetric and isothermal measurements (Table 1). An interesting phenomenon is, that contrary to PNa, ANa is stable at 420°C but the rate of decomposition and ketone formation is much slower for ANa than for PNa in the mixture of these salts. This observation shows that a reaction between decomposition and unconverted material is to be taken into account.

Table 1.

Decomposition parameters of the starting salts

Salts ^a	Decomposition temp. °C		Isothermal measurements at 430°C for one hour	
	Initial	DTG peak	Conversion of salt	% Cp/Ch ^b
ANa	440	480	0	-
PNa	410	500	70	-
ANa PNa (1:1)	400	480	90 40	3.2

^aAbbreviations: ANa: disodium acipate; PNa: disodium pinelate.

^bCp/Ch: Ratio of cyclopentanone and cyclohexanone formed

The exchange data of carboxyl groups (Table 2) point to the different features of two practically identical transformations. This manifests itself in the different incorporation of the carboxyl group arising from the other salt into the residual acids and ketones formed. The data given in Table 2. for ANa do not satisfy the conditions of Buhler's mechanism. In this case, contrary to the data for PNa, the exchange observed in cyclopentanone was considerably higher than in the recovered adipic acid i.e. the exchange reaction does not precede the formation of ketone. At the same time it is also known⁶ that under such experimental conditions, no change of radioactivity, i.e. no exchange after ketone formation can be observed in cyclopentanone. These considerations support the assumption that cyclopentanone formation and carboxyl group exchange proceed through a common intermediate.

Table 2

Exchange data of carboxyl groups

Salt mixture ^a mole ratio: 1:1	Temp. °C	Time min.	Conversion of salt %	Radioactivity (10^5 cpm/ml)			Exchange ^b %	
				Initial acid	Residue acid	Ketone formed	Acid	Ketone
ANa- ¹⁴ C PNa	430	60	90 40	23.00 0	22.52 7.45	9.81 1.22	4.2 64.8	29.4 21.2
ANa- ¹⁴ C PNa	430	30	75 20	23.00 0	22.90 6.00	10.10 0.57	1.7 52.2	24.5 9.9
ANa FNa- ¹⁴ C	430	90	75 20	0 23.1	0.4 19.8	1.61 12.00	2.3 59.1	21.9 14.9
ANa- ¹⁴ C PNa	390	60	0 0	23.00 0	23.00 0	- -	- -	- -

^aAbbreviations: ANa: Acipic acid disodium salt,
FNa: Fimelic acid disodium salt.

^bThese particulars give the extent of equilibrium distribution in percentage.

This common intermediate should contain the carboxyl group of PNa, in a position that allows cyclopentenone formation by incorporation of the carboxyl group.

It seems reasonable to assume that this intermediate is the α -carboxylated product of ANa. Similarly, carboxylation of FNa in the α -position may also be expected. These considerations justified the study of the thermal translocations of pentane-1,1,4-tricarboxylic acid trisodium salt (ENa), and pentane-1,1,3-tricarboxylic acid trisodium salt (FNNa).

As is evident from Table 3. BNa and PNa show different decompositions. In the decomposition of PNa a well-defined second decomposition step can be observed which probably corresponds to the decomposition of PNa formed. The thermal transformation of BNa affords cyclopentanone as the main product, while the same reaction of PNa yields PNa and fails to produce cyclohexanone. Thus, the relatively great difference of exchange data of ANa and PNa (Table 2) can be readily interpreted by the great difference of cyclisation ability of BNa and PNa observed in the thermal transformation process of these salts.

Table 3
Decomposition data of tricarboxylic acid salts

Salts ^a	I s o t h e r m a l m e a s u r e m e n t s								
	decomposition temp. °C						Products formed %		
	Initial	DTG peak	Temp. °C	Time min.	Conv. %	Adipic acid	Pimelic acid	Cyclo-pentanone	Cyclo-hexanone
BNa	400	465	430	60	100	trace	-	60	-
PNa	380	430 500	400	120	100	-	70	-	0

^aAbbreviations: BNa: Butane-1,1,4-tricarboxylic acid trisodium salt;
PNa: Pentane-1,1,5-tricarboxylic acid trisodium salt

In order to verify radioactivity incorporation into cyclopentanone through BNa, butane-1,1,4-tricarboxylic acid(1-carboxy-¹⁴C) trisodium salt was prepared and transformed into cyclopentanone (Fig.3). The complete decomposition of this salt produces cyclopentanone with 25% of the molar activity of the tricarboxylic acid.

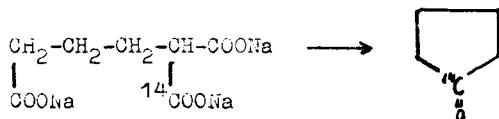


Fig. 3

The formation of such malonate type intermediates cannot be interpreted on the basis of Bühler' mechanism, but can be easily deduced from the mechanism (Fig. 4) proposed by Neunhoeffer and Paschke⁷. α -Carbanions may obviously, participate not only in ketone formation but also in various processes, viz. carboxylation and hydrogen splitting⁸⁻¹⁰ reactions.

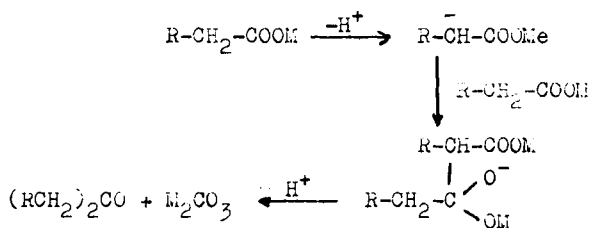


Fig. 4

The carboxylation process yields malonate type products (Fig. 5) unstable at the reaction temperature (Table 5),

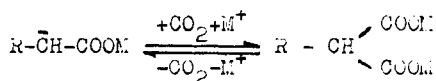


Fig. 5

and are transformed into the starting salt after decarboxylation and subsequent proton abstraction (Fig. 6). In our interpretation the exchange of carboxyl groups takes place in the reaction of

Fig. 5.

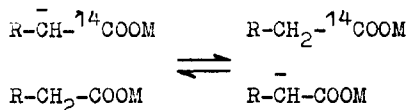


Fig. 6

According to the concept discussed above the exchange reaction proceeds with participation of carbon dioxide. Consequently, an exchange between carboxyl groups and $^{14}\text{CO}_2$ is to be expected. The experimental results collected in Table 4 show significant $^{14}\text{CO}_2$ incorporation with a similar pattern observed for the exchange of carboxyl groups (Table 2). The results are in good agreement with the mechanism proposed above. At the same time, these observations point to the practical importance of this exchange reaction in the field of isotopic tracer techniques. A detailed study of the reaction is in progress in our laboratories.

Table 4

 $^{14}\text{CO}_2$ incorporation data

Salt ^a	Temp. °C	Time min.	Conv. %	Radioactivity 10^6 dpm/ml.		Exchange ^c %	
				acid	ketone	acid	ketone
PNa + $^{14}\text{CO}_2$	$\frac{b}{440}$	60	72	0,711	0,920	20,8	43,0
	$\frac{b}{450}$	60	35	0,300	1,360	23,4	79,6
PNa + $^{14}\text{CO}_2$	$\frac{b}{410}$	120	40	0,343	0,101	18,8	5,9
	$\frac{b}{420}$	120	59	1,380	0,150	40,4	8,8

^a Abbreviations are same as in Table 1.

^b The composition of mixture: 10 mM salt, 2 mM $^{14}\text{CO}_2$ (spec.act. $1.88 \cdot 10^7$ dpm/ml)

^c These particulars give the extent of equilibrium distribution in percentage.

EXPERIMENTAL

Sodium salts were prepared by neutralisation of aqueous solution (or suspension) of the acids with an equivalent amount of NaOH. The solution was evaporated to dryness and dried in vacuo at 200 °C for 2 hours. Purity of the products was checked by Na analysis.

Adipic acid-1,6-¹⁴C₂, and pinelic acid-1,7-¹⁴C₂ were obtained from the respective α, ω -dibromo alkane and K¹⁴CN by a method described by R.J.Speer et al.¹¹ Butane-1,1,4-tricarboxylic acid and pentane-1,1,2-tricarboxylic acid were prepared according to the procedure of L.C.Cheney et al.¹²

Butane-1,1,4-tricarboxylic acid-1,1-carboxyl-¹⁴C₁

Malonic acid — 1-¹⁴C₁ was prepared from chloroacetic acid and K¹⁴CN following the procedure described by E.M.Gal et al.¹³ and then esterified.¹⁴ The synthesis was further carried out by an analogous method used for the radioactive sample. Yield: 47 % (based on K¹⁴C) m.p.: 139-140 °C.

Methods for the study of carboxyl exchange reactions

The reaction conditions were chosen on the basis of derivatogram recorded by a LOM type, Huey-Paulik derivatograph in N₂ stream (15 l/hr). Results are given in Tables 1 and 3.

The decomposition of salts was performed in a metal bath thermostat, working with ± 2 °C accuracy in the temperature range applied. The mixture of ANa-¹⁴C + PNa and ANa + PNa-¹⁴C (mole ratio: 1:1) was decomposed in nitrogen stream (5 l/hr). The cyclopentanone and cyclohexanone formed were condensed in a trap cooled to -80 °C, then analyzed and separated by a gas chromatograph (CARLO ERBA type). For radioactivity determinations, the pure components were converted into the respective semicarbazones, then purified by crystallization.

Radioactivity was determined by a PACKARD TRI-CARB Liquid Scintillation Spectrometer.

The solid residue was dissolved in water and a measured amount of PNa and ANa was added to the aliquot part for the determination of the conversion by the isotope dilution method. The aqueous solutions were acidified with concd. HCl to pH 1, then evaporated to dryness. The carboxylic acids were extracted from the solid residue with hot ethyl acetate. The ethyl acetate solutions were evaporated and the pimelic acid was extracted with hot benzene. On cooling, the pimelic acid precipitated from the benzene solution was recrystallized several times. The adipic acid, which is not soluble in benzene, was recrystallized from concd. nitric acid. Purity of the samples thus obtained was checked by m.p. and C-H analyses. Radioactivity of the acid samples was determined by a method identical with that applied for the semicarbazone samples (Table 2).

The exchange reaction of carboxyl groups and CO_2 carried out under $^{14}\text{CO}_2$ pressure (about 3 atm.) was studied in the following way: $^{14}\text{CO}_2$ (2 ml.) was distilled with liquid nitrogen to the sodium salt in a tube. The tube was sealed, placed in a thermostat and kept at an appropriate temperature. The system was opened and $^{14}\text{CO}_2$ recovered in the form of BaCO_3 . The ketone formed was extracted with ether. Further procedures and measurements were carried out as described above (Table 4).

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