

**TRANSCARBOXYLATION REACTIONS OF SALTS OF ORGANIC ACIDS. XIX.\*****THE EFFECT OF VARIOUS CATIONS ON THE COURSE OF TRANSCARBOXYLATION AND THE CATALYTIC EFFECT OF SOME OF THESE CATIONS**

J. RATUSKÝ

*Institute of Organic Chemistry and Biochemistry,  
Czechoslovak Academy of Sciences, Prague 6*

Received August 10th, 1971

The probable mechanism of the catalytic effect of cations of metals belonging to the group 2b of the periodic system, particularly of cadmium and zinc, was proposed on the basis of a comparison of transcarboxylations of salts of a carboxylic acid with various cations assuming the transcarboxylation mechanism to be an intermolecular ionic decarboxylation-recarboxylation combined with intermolecular transprotonation. The causes of formation of different products in the presence of different cations or inert fusing agents were explained.

The carboxylations of salts of aromatic carboxylic acids have been carried out mainly using potassium as cation. It is, however known, that salts of other metals such as alkali metals, metals of alkali earths or metals of the group 2b of periodic table may also undergo transcarboxylation<sup>1-6</sup>. The kind of cation affects substantially both the reaction course and the yield of the end product. The effect of the cation on the transcarboxylation course, was, save some exceptions, hitherto not studied in detail, although salts of some metals are powerful transcarboxylation catalysts<sup>7,8</sup>. In this communication we turned our attention to transcarboxylation of salts of carboxylic acids where the cations were systematically changed. For the sake of simplicity, we have chosen predominantly the salts of benzene carboxylic acids.

The successful transcarboxylation of aromatic carboxylic acids salts depends on several factors<sup>9-11</sup>: 1) At the reaction conditions, the salt of the transcarboxylated acid must be able to form the corresponding carbanions by splitting off carboxylate groups or protons; 2) except for the reacting salts of acids, the reaction mixture must not contain any further compounds able to liberate protons which would decarboxylate the reacting salts; 3) the salts of the starting acids, as well as of the intermediates and the end-products, must be thermally stable under reaction conditions and, moreover, the end-product must exhibit high crystallization ability; 4) the reaction mixture must be free of any compounds capable of chemical or catalytic action

\* Part XVIII: This Journal 37, 2436, (1972).

TABLE I

Transcarboxylation Reactions of Benzene Carboxylates Containing Various Cations

No	Salt <sup>a</sup>	M.p. °C	Reaction conditions		Yield <sup>b</sup> %	Composition of the mixture of acids <sup>c</sup> , %						
			min	°C		MB	DMT	DMI	DMP	TMTs	TMTl	TMHe
1	B Li	>460	60	450—460	12.0	12.0	73.0	9.0	6.0	—	—	—
2	P Li <sub>2</sub>	>460	60	450—460	15.0	9.5	74.0	8.5	6.5	—	—	—
3	I Li <sub>2</sub>	>460	60	450—460	14.5	10.0	68.5	15.0	7.5	—	—	—
4	B Na	440—450	60	450—465	58.0	26.0	25.5	9.5	6.5	31.0	2.0	0
5	P Na <sub>2</sub>	440	60	450—465	51.5	4.0	29.0	5.0	25.5	34.0	2.4	0
6	I Na <sub>2</sub>	>450	60	450—465	61.5	10.5	29.5	45.0	1.6	12.6	1.3	0
7	T Na <sub>2</sub>	>500	60	465	97.0	0.4	98.8	0.2	0.3	0.5	0	0
8	B K	425	5	405—415	93.0	3.0	89.4	2.9	3.1	0.6	0.9	0.2
9	P K <sub>2</sub>	395—410	5	370—390	91.5	2.1	91.4	3.0	2.1	0.9	0.9	0.2
10	I K <sub>2</sub>	460—465	10	410—425	92.0	3.0	89.1	3.5	2.5	0.9	1.2	0.3
11	T K <sub>2</sub>	>500	30	435	96.5	0.5	98.6	0.3	0.2	0	<sup>d</sup>	0
12	B Rb	380—390	5	360—395	71.4	13.0	57.5	19.0	5.5	1.5	1.9	0
13	P Rb <sub>2</sub>	350—360	3	345—390	69.5	12.4	46.8	19.8	3.3	7.9	9.7	0
14	I Rb <sub>2</sub>	375—390	5	360—400	75.0	11.5	50.7	18.5	4.5	6.5	8.0	0
15	B Cs	350—355	4	370—420	72.5	16.0	19.8	37.3	7.5	8.3	11.2	1.2
16	P Cs <sub>2</sub>	330—335	10	330	68.0	6.6	45.9	48.0	6.7	<sup>d</sup>	<sup>d</sup>	<sup>d</sup>
17	I Cs <sub>2</sub>	325—340	10	350	71.0	8.0	39.0	53.0	6.5	<sup>d</sup>	<sup>d</sup>	<sup>d</sup>
18	B (Ba/2)	—	30	430	59.0	15.5	9.5	13.0	46.5	1.5	6.5	5.0
19	P Ba	—	30	430	58.0	9.5	5.1	6.5	49.0	2.5	10.5	16.5
20	I Ba	—	30	430	62.5	11.0	6.0	16.5	10.5	6.5	22.0	26.5
21	B (Cd/2)235	—	15	300	62.7	85.9	1.07	5.1	6.15	1.69	0.1	0
22	B (Cd/2)235	—	0.3	340—370	48.0	31.6	8.85	45.8	14.35	—	—	—
23	B (Cd/2)235	—	10	270—340	50.0	46.5	8.0	25.0	14.8	1.74	2.25	0.27
24	P Cd	280	6	328—372	35.6	31.2	22.4	21.2	25.0	0	0	0
25	I Cd	—	15	375—400	54.0	29.5	7.9	50.0	11.5	1.0	0.8	0
26	T Cd	—	30	425	51.0	15.5	62.5	11.5	10.0	<sup>d</sup>	<sup>d</sup>	<sup>d</sup>
27	P NaK	—	60	440	71.0	10.5	70.5	8.0	5.5	2.0	2.4	0.7

<sup>a</sup> Abbreviations: The first letter in the symbol of salt denotes: B, P, I, T benzoate, phthalate, isophthalate and terephthalate, respectively; Li, Na, K, Rb, Cs, Ba, Cd, NaK denote lithium, sodium, potassium, rubidium, caesium, barium, cadmium and sodium-potassium cations, respectively, of the corresponding salt. The reaction were carried out in millimolar amounts in sealed glass ampoules, except for experiments 1—7, 18—20 and 27 which were carried out in an autoclave with 0.01 mol of the salt. The amount of Cd<sup>2+</sup> in experiments 1—20 and 27 was 3% (w/w), in the others 0%, CO<sub>2</sub> pressure in experiments 1—7, 18—20 and 27 50 atm, in experiments 8—17 and 21—26 3 atm. <sup>b</sup> Weight % of acids. <sup>c</sup> The analyses of the mixtures of acids were carried out by vapour phase chromatography of their methyl esters; the abbreviations of the esters are given in Table II. <sup>d</sup> Traces.

on the reacting salts, such as *e.g.* oxidants or reducing agents, compounds catalyzing side-reactions, reactive substituents attached to the molecules of carboxylic acids *etc.*; 5) the reaction is facilitated by the presence of suitable catalysts; 6) the course of the reaction depends on the structure of the reacting carboxylic acids since in certain cases their structure determines the ability of transfer of carboxylate groups, and 7) the course of the reaction depends on the kind of cation which strongly affects the fusibility of the mixture during the reaction, as well as the crystallization ability of the end-product. We have shown earlier<sup>9-18</sup> that the transcarboxylation reaction of potassium salts of all aromatic carboxylic acids follows the same mechanism of intermolecular ionic decarboxylation-rearboxylation combined with an intermolecular transprotonation.

From a comparison of results in Table I (experiments 1-17, 27) it follows that transcarboxylation reactions of alkali metal salts of benzene carboxylic acids give highest yields of terephthalate as end-product with potassium cations (Table I, experiments 8-11). On the other hand, in the case of lithium and sodium salts both the starting compounds and intermediates have too high melting points and require therefore substantially higher reaction temperature at which the reaction mixture undergoes appreciable thermal destruction (Table I, experiments 1-7). In the case of rubidium and caesium salts where the transcarboxylation takes place at a relatively low temperature, the observed lower yields are the result of a low crystallization ability of the corresponding terephthalate and a low thermal stability of all these salts, the reaction giving rise to an appreciable amount of tars (Table I, experiments 12-17). Even potassium salts of benzene carboxylic acids may behave similarly if the crystallization of terephthalate from the reaction mixture is prevented by addition of a chemically inert fusing agent such as cyanate or thiocyanate; in this case the end-product consists of a mixture of potassium benzene carboxylates, even when potassium terephthalate was used as starting compound<sup>12</sup>. (Table II, experiments 1-9).

The transcarboxylation of sodium salts of benzene carboxylic acids in the presence of sodium iodide gives, instead of terephthalate, sodium trimesate accompanied with minor amounts of other benzene carboxylates (Table II, experiments 10 to 16). The addition of sodium cyanide or a mixture of sodium and potassium chlorides to the reaction mixture affects the transcarboxylation of sodium benzene carboxylates in a similar manner (Table II, experiments 18, 19). It is evident from the course of transcarboxylation of potassium salts of aromatic carboxylic acids that the first stage of the reaction is the formation of *ortho*-derivatives which are subsequently transformed into *meta*- and finally into *para*-derivatives which crystallize from the reaction mixture<sup>9-11</sup>. Thus, *e.g.* potassium benzoate gives primarily phthalate, then a mixture of hemimellitate and trimellitate, then isophthalate, trimesate, and finally, potassium terephthalate. However, if calcium, strontium or barium salts are used the transcarboxylation stops mainly already at the stage of derivatives with *ortho*-carboxyl groups<sup>1,22</sup>. Thus, strontium and barium benzoates afford predominantly strontium and barium phthalate, respectively (Table I, experiment 18), calcium benzoate gives a mixture of calcium phthalate and isophthalate<sup>1,22,23</sup>, barium

TABLE II  
 Composition of the Reaction Mixtures in Transcarboxylation of Alkali Metal Benzene Carboxylates in Various Fusing Agents<sup>a</sup>

No	Salt	Fusing agent (%) <sup>b</sup>	Time min	T °C	pCO <sub>2</sub> atm	Products, mol % <sup>c</sup>		Composition mixture of acids <sup>d</sup> , mol %						
						acids	B	MB	DMT	DMI	DMP	TMTs	TMTI	TMHe
1	PK <sub>2</sub>	KCNO (400)	8	400	3	94.0	0	19.0	18.0	35.5	5.0	9.0	11.0	1.0
2	IK <sub>2</sub>	KCNO (400)	16	400	3	96.5	0	18.5	17.5	34.0	5.0	9.0	11.5	1.5
3	TK <sub>2</sub>	KCNO (1500)	30	425-450	3	92.0	<sup>e</sup>	21.0	17.0	34.0	5.0	10.0	11.5	1.0
4	BK	KCNO (400)	16	400	3	93.5	88.0	19.5	18.5	33.0	5.0	10.0	11.5	0.5
5	PK <sub>2</sub>	KSCN (500)	4	315-429	3	93.0	0	17.8	0.6	6.4	59.0	0.3	7.95	7.95
6	PK <sub>2</sub>	KSCN (500)	2.5	410	3	89.0	0	17.0	18.5	34.5	7.5	10.0	11.0	1.5
7	IK <sub>2</sub>	KSCN (500)	2.5	410	3	93.0	0	16.5	19.0	35.0	6.5	8.5	12.0	1.5
8	TK <sub>2</sub>	KSCN (1500)	2.5	420-440	3	91.0	0	19.0	18.5	34.5	6.0	9.0	11.0	1.0
9	BK	KSCN (500)	2.5	410	3	89.0	87.0	20.5	17.5	35.5	5.5	8.5	12.5	0.5
10	PNa <sub>2</sub>	NaI (46)	120	440	40	—	—	—	—	—	—	87.0	—	—
11	INa <sub>2</sub>	NaI (46)	120	460	40	—	—	—	5.0	5.7	—	83.0	—	—
12	TNa <sub>2</sub>	NaI (46)	120	460	40	—	—	—	4.8	—	—	93.0	—	—
13	BNa	NaI (33)	120	440	40	—	—	—	3.0	—	—	86.0	—	—
14	PNa <sub>2</sub>	NaI (100)	60	400	30	—	—	—	—	—	—	40.2	—	—
15	PNa <sub>2</sub>	NaBr (100)	60	430	30	—	—	—	—	—	—	16.0	—	—
16	TNa <sub>2</sub>	NaI (100)	60	450	30	—	—	—	—	—	—	<sup>e</sup>	—	—
17	PNa <sub>2</sub>	NaI (46)	120	440	3	71.0	106.7	4.2	23.1	11.7	5.5	49.3	3.3	0
18	PNa <sub>2</sub>	NaCN (100)	120	440	3	38.0	92.0	0.9	9.6	7.0	1.4	75.5	5.5	0.1
19	PNa <sub>2</sub>	KCl (50) + NaCl (50)	60	430-440	3	89.0	35.0	4.7	15.5	5.0	15.0	57.4	2.2	0.2

<sup>a</sup>Abbreviations: the same as in Table I; MB, DMT, DMI, DMP, TMTs, TMTI, TMHe methyl esters of benzoic, terephthalic, isophthalic, phthalic, trimelic, trimellitic and hemimellitic acids, respectively; the experiments 1-9, 17-19 were carried out in sealed glass ampoules in millimolar amounts; catalyst CdI<sub>2</sub>. <sup>b</sup>mol %, in experiments 10-13 weight %. <sup>c</sup>Products denote mol % of benzene (B) and the sum of all acids isolated from the reaction mixture; the difference from 100% represents carbonised and other products. <sup>d</sup>The mixture of acids was analysed by vapour phase chromatography in the form of methyl esters. <sup>e</sup>Traces.

$\alpha$ -naphthoate is transformed into barium 1,2-naphthalenedicarboxylate<sup>6</sup>, barium  $\beta$ -naphthoate affords a mixture of barium 1,2- and 2,3-naphthalenedicarboxylates with the latter predominating<sup>6</sup>, and the reaction of barium isophthalate results in a mixture of barium hemimellitate and trimellitate (Table I, experiment 20) (*cf.* a German patent<sup>1,24</sup> which describes the exclusive formation of hemimellitate); in all these cases the salts of products possess high crystallization ability and are difficult to fuse, and therefore they crystallize from the reaction mixture. The cause of the different behaviour of sodium  $\alpha$ - and  $\beta$ -naphthoates is similar: transcarboxylation of the  $\alpha$ -isomer affords predominantly 2,6-naphthalenedicarboxylate while the  $\beta$ -isomer gives sodium 2,3-naphthalenedicarboxylate, whereas the potassium salts give in both cases the 2,6-isomer<sup>5</sup>. However, the results of the reactions of the above mentioned salts are not so unequivocal as those found for the potassium salts where the intermediates as well as the end-product exhibit properties most favourable for the formation of a single product. It follows from the above mentioned results

TABLE III

Comparison of Melting Points and of the Observable Beginning of the Transcarboxylation Reaction of Potassium and Cadmium Benzene or Naphthalene Carboxylates<sup>a</sup>

No	Salt	M.p., <sup>b</sup> °C	Beginning of transcarboxylation <sup>c</sup>	
			°C	min
1	BK	425—430	420—440	2
2	BCd/2	235	283—288	0.5
3	PK <sub>2</sub>	375—390	403—437	2.5
4	PCd	363 (dec.)	280—290	2
5	IK <sub>2</sub>	464—465	463—465	2
6	ICd	365 (dec.)	375—400	15
7	TK <sub>2</sub>	500	<sup>d</sup>	—
8	TCd	400 (dec.)	425	30
9	$\alpha$ -NaK	248—251	466—470	1
10	$\alpha$ -Na(Cd/2)	217—219 (255—263)	(240)—322	1
11	$\beta$ -NaK	365	466	1
12	$\beta$ -Na(Cd/2)	168—170	277—287	1

<sup>a</sup> Abbreviations: the same as in Table I;  $\alpha$ -;  $\beta$ -NaK and Na(Cd/2) potassium and cadmium  $\alpha$ -; or  $\beta$ -naphthoate, respectively. <sup>b</sup> M.p. up to 370°C were determined on a Kofler block, for higher temperatures a calibrated thermocouple sealed together with the sample in a glass ampoule was used. <sup>c</sup> The determination of temperature and time of the transcarboxylations see <sup>b</sup>. Good observation was achieved in the case of monocarboxylic acids where the escape of the hydrocarbon was easily detected under microscope as intensive movement of the melt. In sealed ampoules the reaction manifests itself by foaming. The reaction conditions of experiments 6 and 8 (Table V).

<sup>d</sup> Does not change up to 460°C.

that the course and result of transcarboxylation of salts with different cations is determined by the effect of these cations on fusing ability, crystallization ability, thermal stability and on the ability of these salts to form carbanions by splitting off the carboxylate groups and protons, these properties being different for salts with different cations.

Also the catalytic effect of zinc and particularly of cadmium salts may be connected with these factors. We studied therefore the transcarboxylations of zinc and cadmium salts of aromatic carboxylic acids which, besides the inorganic salts of these metals, are the best transcarboxylation catalysts. We found that transcarboxylation of cadmium benzene carboxylates follows the same mechanism as the reaction potassium salts. The reaction course is, however, different and resembles rather the reactions of benzene carboxylates of alkali earths, the only difference being the far lesser thermal and transcarboxylation stability of the cadmium salts. Also the melting points and the transcarboxylation temperature of the cadmium salts are substantially lower. Thus, *e.g.* potassium benzoate melts at about 425–430°C (Table III, experiment 1); at this temperature the rate of its transcarboxylation in the absence of catalyst is very low (Table IV, experiments 44–48 or 49–51) and even in the presence of a catalyst the transcarboxylation proceeds rapidly only at temperatures as high as 400°C (Table IV, experiments 52–55). On the contrary, cadmium benzoate melts at 235°C (Table III, experiment 2) and its measurable transcarboxylation begins already at temperatures above 270°C (Table V, experiments 1–3). Similar, though smaller, differences between potassium and cadmium salts are observed for other benzene carboxylic acids (Table III, experiments 3–8; Table IV, experiments 1–26, 29–43; Table V, experiments 4–10).

The transcarboxylations of potassium, rubidium or caesium salts take place even without a catalyst,\* the reaction course and mechanism being the same as in the presence of catalysts, only the reaction being slower. Thus *e.g.* on heating potassium phthalate without catalyst to 340°C, no chemical transformations occur from 30 up to 240 min (Table IV, experiments 1–3) whereas on heating to 435°C transcarboxylation reactions take place in the interval 30 to 360 min, analogously to the reaction in the presence of catalysts (Table IV, experiments 4–8), the overall yield of acids decreasing substantially with prolonged reaction time and higher temperature (Table IV, experiments 1–3, *cf.* experiments 4–8). In order to evaluate the effect of catalysts we heated potassium phthalate in the presence of cadmium iodide. As evident from experiments 9–11 in Table IV, already 0.3% (wt/wt)  $\text{Cd}^{2+}$  accelerates the reaction to such an extent that after 5, 10 and 20 min at 340°C the reaction mixture has the same composition as without catalyst at 435°C after 30, 60 and 120 min (Table IV, experiments 4–6). Naturally, at lower temperature and in a shorter reaction time the side reaction do not occur and therefore in the presence of a catalyst the overall yield of acids is substantially higher than the yield without catalyst (Table IV,

\* First transcarboxylations without catalysts were carried out by von Richter<sup>25</sup>, Wislicenus<sup>26</sup> and Schrader and Wolter<sup>27</sup> who heated benzoate until it carbonized and obtained thus small amounts of isophthalic and terephthalic acids. Similar experiments were carried out by Raecke<sup>1</sup> and later (with potassium isophthalate) by Kružalov and coworkers<sup>28</sup>. Nobody of these authors studied the mechanism of the transcarboxylation reaction.

TABLE IV

Composition of Reaction Mixtures in Transcarboxylations of Potassium Benzene Carboxylate in the Presence or Absence of  $\text{CdI}_2$  Catalyst and under Various Reactions Conditions<sup>a</sup>

No	$\text{CdI}_2^b$	Time min	$T, ^\circ\text{C}^b$	Acids <sup>c</sup> mol %	Composition of mixture of acids <sup>d</sup> , mol %						
					MB	DMT	DMI	DMP	TMTs	TMTI	TMHe
Potassium phthalate											
1	0	30.0	340	98.0	0	0	0	100	0	0	0
2	0	60.0	340	97.0	0	0	0	100	0	0	0
3	0	240.0	340	95.0	0	0	0	100	0	0	0
4	0	30.0	435	78.0	8.75	0	3.75	78.0	0	5.05	4.6
5	0	60.0	435	85.7	26.0	1.9	8.1	39.4	7.1	11.9	5.6
6	0	120.0	435	69.5	22.0	4.5	15.0	35.0	8.4	11.1	4.0
7	0	240.0	435	54.1	12.3	36.7	30.6	8.2	6.9	5.5	0.4
8	0	360.0	435	13.5	22.6	52.7	in DMT	1.6	9.0	12.5	1.5
9	0.3	5.0	340	94.5	14.1	0.4	3.35	68.05	1.2	4.6	8.1
10	0.3	10.0	340	95.0	23.4	1.4	8.5	43.6	2.0	6.5	5.0
11	0.3	20.0	340	96.5	32.0	4.4	10.9	20.7	9.5	14.8	7.8
12	3.0	0.1	330–350	96.0	15.9	0.9	8.2	62.1	1.7	4.5	6.9
13	3.0	0.2	355–373	94.5	23.1	traces	7.2	46.5	0.7	13.6	8.7
14	3.0	0.3	340–379	93.8	33.0	1.6	9.0	23.2	3.0	16.9	13.0
15	3.0	0.5	356–384	92.5	27.5	4.0	23.6	19.5	6.85	16.5	2.5
16	3.0	0.75	395–412	93.0	31.0	9.1	14.5	14.0	8.5	14.0	7.5
17	3.0	0.8	385–408	95.0	26.4	15.5	20.4	11.3	7.1	13.0	6.0
18	3.0	0.9	370–404	92.5	20.8	28.4	17.0	13.0	7.5	13.4	1.0
19	3.0	1.0	370–400	94.0	19.5	47.3	7.5	5.5	8.1	10.0	1.8
20	3.0	1.5	399–417	92.5	0.6	90.1	3.0	5.3	0.5	0.6	—
21	3.0	2.0	386–417	93.8	1.2	87.4	3.4	5.9	0.9	1.1	0.2
22	3.0	4.0	390–410	94.2	5.3	85.3	1.9	2.3	2.0	2.9	0.1
23	3.0	30.0	290–295	98.5	1.3	0.3	1.1	97.3	0.1	0.5	0.3
24	3.0	60.0	290–295	97.0	7.7	4.4	3.3	76.0	2.6	3.1	1.9
25	3.0	120.0	290–295	98.0	8.0	7.0	4.9	67.9	6.0	3.2	3.0
26	3.0	20.0	350–355	91.0	6.0	79.5	4.5	5.1	1.9	2.5	0.5
27 <sup>e</sup>	100.0	60.0	400–410	14.5	15.5	25.5	30.0	15.5	3.6	4.8	2.0
28 <sup>e</sup>	100.0	60.0	400–410	89.5	3.5	87.5	3.0	4.0	0.5	1.0	0.2
Potassium isophthalate											
29	0	30	390	98.0	0	0	100	0	0	0	0
30	0	60	390	97.0	0	0	100	0	0	0	0
31	0	120	390	99.0	0	0	100	0	0	0	0
32	0	30	460	82.5	9.9	5.5	71.0	4.5	3.9	5.1	0
33	0	60	460	77.0	19.4	22.4	34.1	8.35	6.0	8.9	1.8
34	0	90	460	36.4	4.0	87.7	4.1	1.7	0.5	1.1	0
35	0	90	475	29.15	1.7	95.5	0	1.1	0	0.5	0
36	3.0	20	355–358	99.0	traces	0	100.0	0	0	0	0

TABLE IV  
(Continued)

No	CdI <sub>2</sub> <sup>b</sup>	Time min	T, °C <sup>b</sup>	Acids <sup>c</sup> mol %	Composition of mixture of acids <sup>d</sup> , mol %						
					MB	DMT	DMI	DMP	TMTs	TMTI	TMHe
37	3.0	0.1	390—400	98.5	0.6	1.0	98.6	0	0	0	0
38	3.0	0.5	400—410	99.0	21.5	6.8	46.8	3.1	7.0	14.0	0.5
39	3.0	5	400—405	97.5	4.0	62.3	26.4	2.5	2.8	3.0	0
40	3.0	1	420—440	96.0	17.0	12.3	51.0	2.3	7.0	10.6	0.5
41	3.0	1.5	420—440	96.4	10.0	39.3	33.4	6.4	3.8	6.6	0
42	3.0	3	420—440	95.1	2.7	83.0	4.6	4.6	2.1	3.0	0
43	3.0	4	420—440	95.5	0.3	88.7	5.0	5.4	0.4	0.6	0
Potassium benzoate											
44	0	2	420—440	—	98.3	0.1	0.4	1.2	0	0	0
45	0	4	420—440	—	97.7	0.2	0.5	1.5	0	0	0
46	0	3	430—450	—	94.5	0.9	1.9	2.6	0	0	0
47	0	4	430—450	—	93.5	0.9	2.1	3.7	0.05	0.01	0.02
48	0	10	430—450	—	90.1	1.4	3.5	4.2	0.04	0.3	0.2
49	0	30	450	50.7	39.0	14.7	22.2	22.9	0.9	0.8	0
50	0	60	450	31.5	6.1	83.0	4.8	4.3	0.7	1.1	0
51	0	120	450	29.0	3.9	85.5	4.3	4.5	0.6	0.8	0
52	3.0	0.5	390—400	—	73.6	6.6	7.0	11.2	0.4	0.7	0
53	3.0	1	390—410	—	45.6	27.1	13.6	13.4	0.8	0.7	0
54	3.0	2	395—400	92.5	13.7	51.6	12.5	22.1	0.6	0.9	0
55	3.0	5	395—425	91.0	0.9	90.0	2.1	7.0	0	0	0

<sup>a</sup> Abbreviations see Table I and II; the reactions were carried out in millimolar amounts in sealed ampoules under 3 atm CO<sub>2</sub>. <sup>b</sup> Given as %Cd<sup>2+</sup> per weight of the salts; because of the short reaction time the temperature in experiments 12—22, 37—48 and 52—55 was not constant and therefore only the range of temperature during the reaction time is given, as the beginning being chosen the moment at which the reaction mixture begins to melt. <sup>c</sup> The yield of acids is given in mol % per amount taken into reaction. The difference from 100% represents carbonised material and losses during isolation. In experiments 44—48 and 52, 53 it is not possible to give the total yield of acids as in the course of the reaction a part of benzoate underwent disproportionation while another part was still unreacted. In the other experiments this yield is given, even though it contains the error mentioned, because in comparison of experiments 49—51 (without catalyst), with experiments 54 and 55 in which the reaction was catalysed, indicates the extent of thermal destruction processes caused by the long reaction time and high temperature. <sup>d</sup> The mixtures of acids were analysed in the form of their methyl esters by vapour phase chromatography. <sup>e</sup> The experiments were carried out in an autoclave under 50 atm CO<sub>2</sub>, using 0.1 mol of phthalate; in experiment 27 an equimolar amount of CdI<sub>2</sub>, in experiment 28 an equimolar amount of powdered metallic Cd, was used as catalyst.





cf. experiments 9–11 and 4–6). The presence of 3% (wt/wt) of  $\text{Cd}^{2+}$  increases further the rate of transcarboxylation to such an extent that at 330–385°C a reaction mixture of approximately the same composition as above (Table IV, experiments 9–11 and 4–6) is obtained after about 0.1–0.5 min (Table IV, experiments 12–15).

Such high yields (about 90%) as obtained in the transcarboxylation of phthalate after 1–2 min in the presence of 3%  $\text{Cd}^{2+}$  (Table IV, experiments 20–22) cannot be obtained without catalyst at all since prolongation of the reaction time results in very diminished yields of acid caused by destructive side-reactions (Table IV, experiments 7, 8). It is necessary to note that these side-reactions may be, at least partially prevented by working under higher pressure of  $\text{CO}_2$ . For further illustration of the catalyst action we may mention the transcarboxylation of potassium phthalate, catalysed by 3%  $\text{Cd}^{2+}$  (wt/wt) at 290–295°C (Table IV, experiments 23–25). As is evident from the experiments, the salt slowly reacts even at this temperature which is the temperature of transcarboxylation of cadmium salts of benzene carboxylic acids (Table III, experiments 2 and 3). This proves that the cadmium benzene carboxylates which arise by the reaction of corresponding potassium salt with inorganic cadmium salt (catalyst) initiate the transcarboxylation reaction of potassium salts thanks to the smooth carbanion formation at low temperatures.

The effect of catalysts is similar also in the reaction of potassium isophthalate (Table IV, experiments 29–43) and benzoate (Table IV, experiments 44–55) the only difference being the higher temperature of the transcarboxylation of potassium isophthalate since this salt has higher melting point. This may be illustrated (Table IV, experiment 36) by the fact that, in the presence of 3%  $\text{Cd}^{2+}$  (wt/wt), the isophthalate does not change after 20 min at 355–358°C whereas the

TABLE V

Composition of the Reaction Mixtures in Transcarboxylation of Cadmium Benzene Carboxylates under Various Reaction Conditions<sup>a</sup>

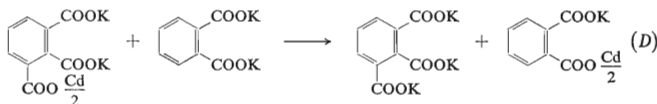
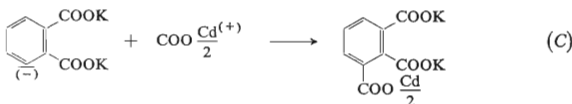
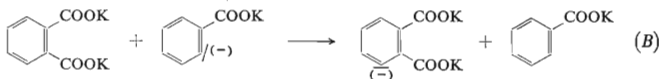
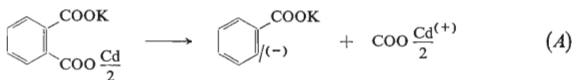
No	Salt	Time <sup>b</sup> min	Temper- ature <sup>b</sup> , °C	Acids <sup>c</sup> mol %	Composition of mixture of acids <sup>d</sup> , mol %						
					MB	DMT	DMI	DMP	TMTs	TMTl	TMHe
1	2 BCd/2	15	280–300	62.7	85.7	1.1	5.1	6.2	1.7	0.1	0
2	2 BCd/2	10	270–340	50.5	46.5	8.0	25.0	14.8	1.7	2.3	0.3
3	2 BCd/2	0.1	340–370	48.6	31.6	8.9	45.8	14.4	0.5	0.5	0
4	PCd	5	285–320	88.9	2.5	0.5	3.0	93.0	0.8	0.8	0.1
5	PCd	60	308–312	96.0	2.2	1.1	3.4	91.2	0.9	1.0	0.4
6	PCd	10	285–350	39.9	13.0	14.0	39.0	18.9	6.5	8.0	0.2
7	PCd	6	328–372	35.6	31.2	22.4	21.2	25.0	not analysed		
8	PCd	10	330–375	21.5	6.5	34.0	37.5	10.5	4.0	7.0	0.3
9	ICd	15	375–400	34.0	29.5	7.9	50.0	11.5	1.0	0.8	0
10	TCd	35	425	51.0	15.5	62.5	11.5	10.0	traces		

<sup>a</sup> Abbreviations and reaction conditions see Table I and II. <sup>b</sup> The reaction temperature measurement was hampered by blackening and decomposition of the reaction mixture and therefore it was difficult to determine the starting point of the reaction (particularly in experiments 3, 6–8). <sup>c</sup> In experiments 1–3 the yield of acids is based on the disproportionation of cadmium benzoate. In all experiments, the difference of mol % from 100 represents carbonised products.

<sup>d</sup> See this footnote in Table IV.

potassium phthalate is transformed under the same conditions almost completely to terephthalate (Table IV, experiment 26).

It follows from the above mentioned results that the catalytic effect of cadmium salts is caused by their ability to form carbanions by a smooth decarboxylation of carboxylate groups, and thus to initiate the reaction of salts of aromatic carboxylic acids according to a reaction sequence such as shown for potassium phthalate, (A)–(D).



In this way, the catalytically active cadmium ion migrates between the molecules of potassium salts of carboxylic acids and we may thus explain the fact that the transcarboxylation reaction proceeds faster if the reaction mixture easily goes over into the molten state (*cf.* the mentioned reactivity difference in transcarboxylation of potassium isophthalate, Table IV, experiment 36, and potassium phthalate, Table IV, experiment 26, which is reversed to the difference between the reactivity of cadmium benzoate and cadmium phthalate, Table V, experiments 1–3 or 4–6).

The course of transcarboxylation of salts of other aromatic carboxylic acids with various cations is analogous to that of benzene carboxylates. Also the catalytic effect of cadmium and zinc salts is similar. Thus, *e.g.* potassium  $\alpha$ -naphthoate melts at 248–251°C and, without catalyst, an observable transcarboxylation begins at 466°C (Table III, experiment 9) whereas cadmium  $\alpha$ -naphthoate has m.p. 217–219°C and begins to react already at 322°C (Table III, experiment 10). Similarly, potassium  $\beta$ -naphthoate has m.p. 410–420°C and begins to react at 466°C (Table III, experiment 11) whereas cadmium  $\beta$ -naphthoate melts at 168–170°C and reacts at 277 to

287°C (Table III, experiment 12). If the transcarboxylation of potassium  $\alpha$ - or  $\beta$ -naphthoate is catalyzed by cadmium salts, the reaction begins already at about 300°C; this is the transcarboxylation temperature of pure cadmium  $\alpha$ - or  $\beta$ -naphthoates. All these examples of transcarboxylation of naphthalene carboxylates are in full accord with the examples shown for benzene carboxylates<sup>15</sup> confirming thus the identical mechanism of these reactions and an analogous catalytic action of cadmium salts in transcarboxylations.

Our proposed mechanism of the catalytic action of inorganic salts of metals of the second group of periodic table is more probable than the mechanism of a "sandwich-like" complex suggested by Ogata and coworkers<sup>7</sup> and by Furuyama<sup>8,29</sup>, since the transcarboxylation of salts of aromatic carboxylic acids follows the same mechanism even in the absence of catalysts. In cases where only negligible quantities of catalyst are present, the "sandwich-like" mechanism would require a perfect mobility of the reacting molecules which can hardly be expected for some salts of carboxylic acids (*e.g.* transcarboxylation of potassium isophthalate) or for some stages of the reaction (*e.g.* in the end stage of transcarboxylation of benzene carboxylates where the reaction mixture contains appreciable amount of terephthalate together with great amount of isophthalate and benzene tricarboxylates, and is solid.).

It is interesting to compare the catalytic activity of catalysts according to their chemical composition or physical state<sup>2,8-10,30-32</sup>. Thus, *e.g.* the catalytic activity of cadmium in the transcarboxylation of potassium benzene carboxylates drops in the following sequence:  $\text{CdI}_2 > \text{CdCl}_2 > \text{CdF}_2 > \text{CdCO}_3 \approx \text{CdO} \approx \text{Cd benzencarboxylate} \gg \text{Cd (powder)} \gg \text{Cd (filings)}$ . The explanation of this difference in reactivity rests in different degree of dispersion of the catalyst in the reaction mixture; *e.g.* for cadmium salts the activity depends on their reaction with potassium benzene carboxylates. This reaction is, naturally, enhanced by good mechanical mixing of the mixture as well as by good fusibility of the reaction components and also by the acidity of the catalyst anion. Therefore, of the cadmium halides the iodide reacts with potassium phthalate more easily than chloride or fluoride, which in turn react better than oxide or carbonate, the reaction being faster with potassium phthalate than with benzoate or isophthalate. This interplay in fusibilities and therefore in the reactivity of cadmium catalysts and potassium benzene carboxylates determines the catalytic activity of cadmium salts as expressed by the above sequence. If already prepared cadmium benzene carboxylates are used as catalyst, they are dispersed only after melting of the reaction mixture; therefore their catalytic activity is lower than that of inorganic salts of cadmium and is roughly comparable with the activity of cadmium carbonate or cadmium oxide. Therefore, in a search for other catalysts which would ensure a better homogeneity and which would readily react with the salts of transcarboxylated acids, various complex cadmium salts, such as *e.g.*  $\text{K}_2\text{CdCl}_2\text{F}_2$  or  $\text{K}_2\text{CdF}_4$  *etc.*<sup>32</sup> were prepared. However, the suggestion of Japanese authors<sup>8,30</sup> that the anion of the catalyst has a specific effect on the course and result

of the reaction is considered by us as improbable. Although the differences in the catalytic activity for all cadmium salts are quite marked, they are not so pronounced as in the case of the last group, *i.e.* the metallic cadmium, either as powder or filings or even in the molten state<sup>2,9,10</sup>. The activity of these catalysts is one to two orders of magnitude lower than the activity of the most active catalyst, *i.e.* than the inorganic cadmium salts, since, in principle, the catalyst is not the metallic cadmium itself but small amounts of oxides or salts formed by corrosion of the surface of the metal grains during storing, or in the transcarboxylation by the action of reactants at high temperature. Therefore when metal powder is used in the reaction, the carbonisation of the transcarboxylated potassium salts is negligible and corresponds to the small amount of cadmium salts on the surface of the metal, even though when the catalyst is applied in a great excess. Contrary to this behaviour of cadmium powder the presence of cadmium salts leads to partial thermal destruction of the transcarboxylated potassium salts due to the considerable thermal lability of cadmium salts of aromatic benzene carboxylic acids (Table IV, experiments 27, 28).

We may conclude that the most frequent transcarboxylations of potassium salts of aromatic carboxylic acids which give *para*-derivatives of these acids, *e.g.* potassium terephthalate, 2,6-naphthalenedicarboxylate, 2,5-pyridinedicarboxylate, *etc.*, represent only a special case of the common course of transcarboxylations. Therefore, it is possible to influence this course by various methods, such as the use of suitable fusing agents or various cations, so as the transcarboxylation leads then to the formation of end products other than the transcarboxylation of potassium salts alone.

## EXPERIMENTAL

*Preparation of samples.* Alkali metal salts of aromatic carboxylic acids were prepared by neutralisation of the corresponding acid with alkali metal hydroxide (phenolphthalein); the solution was evaporated to dryness and the residue was powdered and dried at 120–130°C/0.01 Torr for 10 h.

*Reaction procedure.* A mixture of the reactants in sealed glass ampoules was placed into an electrically heated quartz tube, and worked up and analyzed as described earlier<sup>9</sup>. The melting points of salts were determined either on a Kofler block or in a sealed capillary placed in a test tube, together with a thermometer, in an electrically heated quartz tube. The beginning of the transcarboxylation (reaction temperature and time) was determined by either of the two following methods: 1) In the reaction of aromatic monocarboxylates where the transcarboxylation is accompanied with evolution of bubbles of escaping hydrocarbon, the beginning of the reaction was indicated by foaming, observed either under microscope or in a sealed capillary in a heated quartz tube. 2) In the case of aromatic dicarboxylates where the reaction mixture does not foam, the beginning of the transcarboxylation was determined by analysis of the reaction samples obtained by heating in sealed ampoules. The results of the measurements and analyses are given in the pertinent Tables.

## REFERENCES

1. Raecke B.: *Angew. Chem.* 70, 1 (1958).
2. Šorm F., Ratuský J., Novosad J.: Private communication.
3. Raecke B. (Henkel & Cie): German Pat. 958 023 (1957).
4. Furuyama S., Ebara N.: *Sci. Papers Gen. Educ. (University Tokyo)* 17, 81 (1967).
5. Dozen Y.: *Bull. Chem. Soc. Japan* 41, 664 (1968).
6. McNelis E.: *J. Org. Chem.* 30, 1209 (1965).
7. Ogata Y., Sakamoto K.: *Chem. Ind. (London)* 1964, 749; 1964, 2012.
8. Furuyama S.: *Sci. Papers Gen. Educ. (University Tokyo)* 16, 203 (1966).
9. Ratuský J., Tykva R., Šorm F.: *This Journal* 32, 1719 (1967).
10. Ratuský J., Šorm F.: *Chem. Ind. (London)* 1966, 1798.
11. Ratuský J.: *This Journal* 32, 2504 (1967).
12. Ratuský J.: *This Journal* 33, 2346 (1968).
13. Ratuský J., Tykva R.: *J. Lab. Comp.* 5, 211 (1969).
14. Ratuský J., Tykva R.: *Radiochem. Radional. Letters* 1, 325 (1969).
15. Ratuský J.: *Chem. Ind. (London)* 1970, 1347.
16. Ratuský J.: *This Journal* 36, 2843 (1971).
17. Ratuský J.: *J. Radional. Chem.* 8, 107 (1971).
18. Ratuský J.: *This Journal* 37, 2436 (1972).
19. Henkel & Cie: *Brit. Pat.* 813 182 (1958).
20. Henkel & Cie: German Pat. 1 028 984 (1958).
21. Henkel & Cie: *Brit. Pat.* 816 248 (1959).
22. Raecke B., Schirp H., Blaser B. (Henkel Cie): German Pat. 1 028 984 (1958).
23. Henkel & Cie: *Brit. Pat.* 806 569 (1957).
24. Raecke B., Blaser B., Schirp H. (Henkel & Cie): Austrian Pat. A-1848-57 (1957).
25. von Richter W.: *Ber.* 6, 876 (1873).
26. Wislicenus W., Conrad H.: *Ber.* 6, 1395 (1873).
27. Schrader H., Wolter H.: *Ges. Abb. Kenntn. Kohle* 6, 81 (1921).
28. Kružalov B. D., Chčejan Ch. E., Pavličev A. F.: *Chim. průmyslnost* 1959, 288.
29. Furuyama S.: *Bull. Chem. Soc. Japan* 40, 1212 (1967).
30. Ogata Y., Tsuchida M., Muramoto A.: *J. Am. Chem. Soc.* 79, 6005 (1957).
31. Beránek L., Bažant V.: *Chem. průmysl* 20 (45), 261 (1970).
32. Schütt H. (Henkel & Cie): German Pat. 1 024 503 (1958).

Translated by M. Tichý.