The Decarboxylation of Carboxylic Acids During the Autoxidation of Cyclohexane

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The oxidative decarboxylation of adipic acid does not contribute significantly to the poor selectivity observed during autoxidation of cyclohexane under the conditions examined. The stabilities of adipic, glutaric, succinic, and acetic acids during the cobalt-catalyzed air oxidation of cyclohexane were investigated using carbon[14] tracer methods. The amount and rate of decarboxylation of the various acid products increased rapidly with increasing temperature and cobalt-catalyst concentration. At 90°C, <3% of the adipic acid product decomposed (rate = 2.1% hr^{-1}), and at 150°C >12% of the adipic acid decarboxylated (rate = 50% hr^{-1}). However, at all temperatures, decarboxylation has only a minor effect on overall selectivity. At 150°C glutaric and succinic acids reacted at about 25% of the rate of adipic acid; acetic acid decomposed at about 7% of the adipic-acid rate. Carbon monoxide is also produced in large quantities but does not contain any radioactivity. The rate of decarboxylation did not decrease with increasing hydrocarbon conversion in contradiction to previous literature reports on similar systems.

INTRODUCTION

The autoxidation of cyclohexane has been extensively studied because of the industrial importance of the principle reaction product, adipic acid *(1, 2)*. Molar yields greater than 70% have only rarely been reported

Studies of the decarboxylation of monobasic acids by Lande and Kochi *(3)*, Clifford and Waters *(4)*, and others *(5–11)* have shown that these acids are rapidly decomposed by cobaltic and other metal ions in H_2O and carboxylic acid solvent Eq. (1).

$$R-C\overset{O}{\underset{OH}{\diagdown}} + Co^{3+} \longrightarrow R\cdot + CO_2 + Co^{2+} + H^+ \quad (1)$$
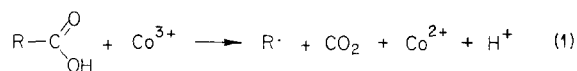
and, in general, were only achieved at relatively low cyclohexane conversion *(1)*. Analyses of the products obtained during the cobalt-catalyzed, air oxidation of cyclohexane show that glutaric and succinic acids constitute a significant percentage of the identifiable products: approximately 20 mole % at 90°C and 50 mole % at 150°C *(1)*. These results suggest that the instability of adipic acid contributes to the poor overall selectivity; however, a variety of side reactions have also been suggested to account for the low yield.

The rapid rates of reaction observed during these earlier studies lead one to speculate that decarboxylation might drastically influence the selectivity of a cobalt-catalyzed autoxidation reaction. However, these results can not be extrapolated to a system involving catalytic autoxidation of hydrocarbons. Difficulties which would prevent such an extrapolation to a system involving the cobalt-catalyzed autoxidation of cyclohexane are: (a) the decarboxylations of adipic, glutaric, succinic, and acetic acids have not been examined; (b) interference

by species which are known to rapidly react with cobaltic ions, e.g., cyclohexanone (12), cyclohexanol (13, 14), a variety of alkyl-, oxy-, and peroxy-free radicals (3, 4, 12–14), H_2O (15, 16), and hydroperoxide (17); and (c) the nature and concentration of the cobaltic catalyst have not been determined.

Several reports have appeared which describe the decarboxylation of carboxylic acids during the autoxidation of neat hydrocarbons (18–23). However, the results of these studies are severely complicated by catalyst precipitation and phase formation which accompany autoxidation in nonpolar media (24). Such complications lead to conflicting conclusions (19). In addition, the early studies do not mention the capability of metal ions to induce decarboxylation even though the related literature strongly suggests that metal ions might be involved (3, 4, 7, 10, 11).

This report describes the oxidative decarboxylation of a variety of carboxylic acids under catalytic-autoxidation conditions to determine the effect of decarboxylation on selectivity.

METHODS

A. Materials

Oxygen and nitrogen were CP grade (Matheson Company). Cyclohexane and cyclohexanone were chromatoquality (99+ mole % pure, Matheson, Coleman, and Bell). Glutaric-1-5-^{14}C and succinic-1,4-^{14}C acids were purchased from Mallinckrodt Chemical Works. Adipic-1,6-^{14}C and acetic-1-^{14}C acids were purchased from New England Nuclear Corp. Cobalt acetate was used as supplied by Fisher Scientific Co. and also after recrystallization from acetic acid with indistinguishable results. Purification of acetic acid, cyclohexane, and cyclohexanone by distillation did not alter the results.

B. Oxidation Procedure and Apparatus

Five μC of the radioactive acid in 2.5 g of acetic acid was added to the starting solution, which was composed of acetic acid (44.5 g, 0.74 moles), cyclohexane (21.0 g, 0.25 moles), and cyclohexanone (0.630 g, 6.4 mmoles). An accurately weighed (~2.0 g) sample of this starting material was retained for radioactivity counting as described below. The remainder of this solution was weighed by difference into the autoclave. Cobalt acetate [$Co(OAc)_2 \cdot 4H_2O$, 0.82 g, 3.3 mmoles] was then added to the reactants.

All experiments were performed in 300 ml stainless steel magnedrive autoclaves (Autoclave Engineers, Erie, Pa.). The reactor was maintained at constant pressure by automatically supplying oxygen from a 100-ml high-pressure reservoir via a solenoid activated by a Foxboro Model 30 pressure transmitter. Progress of the reaction was followed by continuously recording the pressure of the 100 ml high-pressure reservoir. Reaction temperature was continuously measured by internal thermocouples and automatically maintained using a Guardsman electronic temperature controller.

A nitrogen atmosphere, ~20–30 psig, was added to the reactor system which was then heated to reaction temperature. Oxygen, 50 psia, was charged to the autoclave and a variable induction period followed. The beginning of the reaction (time zero) was set as the time oxygen uptake commenced. All experiments were terminated after 0.20 moles of oxygen had been consumed. At 150°C, CO_2 was produced at such a rapid rate that the reactor had to be repressured several times before 0.20 moles of oxygen was reacted. After the required oxygen was consumed, the feed line was closed and the system was allowed to react for ~1 hr to remove any traces of oxygen left in the gas phase. Subsequently, the reactor was cooled to room temperature.

The solubilities of CO and CO_2 in the reaction solution were large and special precautions had to be employed to quantitatively recover these products. The free space above the reaction solution (~190 ml) contained about ⅓ of the CO_2 and most of the CO. A gas sample was collected by venting the reactor into an evacuated 4-liter steel cylinder. The autoclave was repressured with ~30 psia of N_2 and the solution was rapidly agitated (~15 min) to re-equilibrate the CO and CO_2 between the

liquid and the gas phases. The reactor was again vented into the steel cylinder and the procedure was repeated 4 more times.

The cylinder was alternately heated and cooled to insure complete gas mixing and then equilibrated at $25 \pm 1°C$. After determination of the cylinder pressure, a GC analysis of the gas was obtained and the quantity of CO and CO_2 was calculated.

An accurately weighed quantity ($\sim$50 g) of tetrahydrofuran (THF) was then added to the reactor to homogenize the remaining 3 phases of the product mixture (cyclohexane phase, aqueous acetic acid phase, and solid dibasic acid phase). This homogenized sample was discharged into a pre-weighed bottle. Blank experiments show that 3–5 g of an identical synthetic reaction-mix sample ($\sim$120 g) was left in the autoclave by this procedure.

C. Radioactivity Counting Procedures and Apparatus

Each decarboxylation experiment required the determination of the radioactivity of 3 different samples: (i) the starting reaction mixture, (ii) the product mixture, and (iii) the CO_2 and CO. Samples were prepared for radioactivity counting in the following ways:

(i) An accurately weighed portion of the starting reaction mixture ($\sim$2.0 g) was diluted to 50.0 ml with acetic acid. One ml of this diluted sample was added to 15 ml of the "counting solution" which was composed of 5 ml of H_2O and 10 ml of gel phosphor.

(ii) An accurately weighed portion of the homogenized product mixture (2.5 g) was diluted to 50.0 ml with acetic acid and 1.0 ml of this diluted sample was added to 15 ml of the "counting solution."

(iii) Carbon dioxide was isolated and prepared for counting by passing the gas sample through both a NaOH ($2.000 N$) solution and a $BaCl_2$ solution (10% by weight in $0.5 N$ NaOH). A peristaltic pump was used to evacuate the gas-sampling cylinder. If CO was present, the gas from the $BaCl_2$ scrubber was oxidized by CuO at $\sim$350°C and the CO_2 scrubbing procedure was repeated.

The NaOH scrubbing solutions were titrated, after the addition of neutral $BaCl_2$, to determine the amount of CO_2 trapped. The $BaCl_2$ scrubbing solution never produced any $BaCO_3$ precipitate, thus demonstrating the effectiveness of the NaOH solution.

One ml of the NaOH scrubbing solution was added to 15 ml of "counting solution."

Samples, prepared as described above, were counted using a Packard-Tricarb liquid scintillation counter. The counting efficiency of most samples was checked by the method of standard addition ($\sim$700 count/sec). No normalization was necessary. The results reported are the average of 9 or 10 counting periods of 1000 sec each. Background counts from the NaOH solution were determined ($\sim$0.3 counts/sec ml) and substracted from the counts generated by the scrubbing solutions.

RESULTS AND DISCUSSION

The significant results of this work are:

(a) The oxidative decarboxylation of adipic acid represents only a very minor selectivity-loss (less than 4 mole % based on reacted cyclohexane) during the cobalt-catalyzed, autoxidation of cyclohexane in acetic acid.

(b) Under these same conditions, glutaric and succinic acids constituted a significant percentage of the identifiable products, i.e., at 90°C approximately 20 mole % of the analyzed products was either glutaric or succinic acid, at 150°C this rose to almost 50 mole %. (Table 1).

(c) The major routes to glutaric and succinic acids are not via decarboxylation of adipic or glutaric acids.

These conclusions were arrived at in the following manner. In order to determine the amount and rate of decarboxylation during autoxidation, trace quantities ($\sim$0.001 mmoles) of $^{14}CO_2$ labeled carboxylic acids were introduced into a system of oxidizing cyclohexane. The carbon oxides were collected and the radioactivity was determined by standard techniques.

The amount of decarboxylation was calculated by multiplying the percentage of radioactivity in the gas phase by 2 for those

TABLE 1

CYCLOHEXANE OXIDATION: PRODUCT DISTRIBUTION AS A FUNCTION OF TEMPERATURE[a]

Oxygen pressure = 50 psia
Moles of O_2 reacted = 0.20
[Cyclohexane] = 3.3 M
[Cyclohexanone] = 8.6×10^{-2} M
[Co(OAc)$_2$ · 4H$_2$O] = 3.3×10^{-2} M
Acetic acid = 9.75 M

Temp (°C)	Conversion of cyclohexane (%)	(mmoles)	Adipic acid (mmoles)	Glutaric acid (mmoles)	Succinic acid (mmoles)	Cyclohexanol[b] (mmoles)	Cyclohexanone[c] formed (mmoles)	Cyclohexane accounted for (%)	CO$_2$ (mmoles)	CO (mmoles)
90	31.3	77.5	47.7	6.4	6.5	0.0	8.3	88	29	1.7
125	20.6	51.0	36.2	7.5	4.1	0.0	-4.1	85	33.0	8.6
150	15.1	36.7	9.9	9.2	5.0	6.2	-4.	72.3[f]	63.0	33.0
150[d]	26.9	67.6	10.2	3.0	1.7	9.9	17.1	62.1[f]	31.0	35.0
150[e]	13.6	32.9	7.8	7.1	4.1	5.3	-3.9	61.7[f]	71.3	25.0

[a] Results are average of three or more experiments, total volume of the solution is 67 ml.
[b] As cyclohexanol and cyclohexyl acetate.
[c] Six mmoles of cyclohexanone charged to system: Results are cyclohexanone formed.
[d] No catalyst.
[e] Double catalyst concentration.
[f] Several small peaks appeared in this analysis but were not identified.

cases where dibasic acids were employed. These calculations are based on the following assumptions which appear valid in view of the related literature:

1. The acid will not undergo complete degradation following the primary decarboxylation step (3);

2. The extent of decarboxylation is relatively small and, therefore, secondary decarboxylation of a molecule having previously undergone decarboxylation is statistically unfavorable; and,

3. The $^{12}C/^{14}C$ isotope effect is negligible (25).

The percentage of decarboxylation is a function of temperature (Table 2) which, for the carbon^{14} labeled adipic acid, ranges from less than 4% at 90°C to 25% at 150°C. The rate of decarboxylation increases over the same temperature range from 2.1% hr^{-1} to 50% hr^{-1}. (The rate of decarboxylation was estimated by dividing the percentage of decarboxylation by twice the half-life of the reaction.) A kinetic rate constant can not be determined since the actual concentration of the decarboxylating reagent, presumably cobaltic ion, is not

known. For this same reason activation energies and entropies are meaningless.

Separate experiments showed that in the absence of cyclohexane, adipic acid did not decarboxylate under otherwise identical conditions. The amount of decarboxylation was a function of cyclohexane conversion, i.e., after 30% of the oxygen reacted, 30% of the total decarboxylation had taken place (Table 3). The addition of large quantities of adipic acid did not alter the amount of decarboxylation (Table 3). These results are contrary to previous studies in hydrocarbon solvents (18–23) which reported that the rate of decarboxylation decreased with increased conversion. The mechanism proposed to explain the rate-decrease suggested that a carboxylic acid dimer was formed which was particularly stable because decarboxylation proceeded via free-radical abstraction of a hydroxyl-hydrogen (19). This mechanism seems unlikely in view of the work by Szwarc and Smid (26) which demonstrates that free-radicals abstract α- rather than hydroxyl-hydrogens. Alternate explanations for the decrease in rate of

TABLE 2

PERCENTAGE DECARBOXYLATION OF CARBOXYLIC ACIDS

Oxygen pressure = 50 psia [Co(OAc)$_2$ · 4H$_2$O] = 3.3 × 10^{-2} M
[Cyclohexane] = 3.3 M Moles of oxygen reacted = ~0.20
[Cyclohexanone] = 8.6 × 10^{-2} M [Acetic acid solvent] = 9.75 M

Acid	Temp (°C)	Decarboxylation[a] Extent (%)	Rate (% hr^{-1})	Activity balance[b] (%)	Activity as CO (%)
Adipic	90	3.8	2.1	96.	0.0
	125	5.4	6.5	97.	0.04
	150	24.9	50.	98.	0.1
Adipic[c]	150	8.3	17.	98.	0.05
Adipic[d]	150	30.1	60.	98.	0.4
Glutaric	90	2.6	1.8	99.	0.0
	150	13.0	13.	100.	0.08
Succinic	90	2.6	1.3	99.	0.0
	150	12.3	13.	100.	0.08
Acetic	90	0.08	0.4	98.	0.0
	115	0.3	0.3	99.	0.0
	150	1.9	3.6	97.	0.0

[a] Average of 2 or more experiments.
[b] Activity balance = (Activity recovered/activity charged) × 100.
[c] No catalyst.
[d] [Co(OAc)$_2$] = 6.6 × 10^{-2} M.

TABLE 3

AMOUNT OF DECARBOXYLATION OF ADIPIC ACID
AS A FUNCTION OF OXYGEN CONSUMPTION

Oxygen pressure = 50 psia
[Cyclohexane] = 3.3 M
[Cyclohexanone] = 8.6×10^{-2} M
[Co(OAc)$_2$ · 4H$_2$O] = 3.3×10^{-2} M
Temp = 90°C
[Acetic acid solvent] = 9.75 M

Expt.[a]	Oxygen reacted moles[b] (% of standard experiment)	CO$_2$ (mmoles)	Decarboxylation (%)
A	0.06 (30)	8.7	1.6
B	0.20 (100)	29.	3.8
C	0.28 (140)	44.	4.5
D[c]	0.20	32.	3.3
E[d]	0.20	32.	3.6

[a] Average of 3 experiments ± 10%

[b] Reaction stopped by cooling rapidly to 10°C.

[c] Nonlabeled adipic acid added (7.3 g) in addition to radioactive adipic acid.

[d] Nonlabeled adipic acid added (3.9 g) in addition to radioactive adipic acid.

^{14}CO$_2$ formation with increased conversion are that the metal-ion catalyst precipitates from the nonpolar hydrocarbon medium employed during many of the previous studies or that the polar carboxylic acid is extracted into the aqueous phase that forms after a few percent conversion (1). However, since different solvents are employed, no direct comparison can be made.

Calculations show that the decarboxylation of adipic acid represents a loss of only 4% of the reacted cyclohexane even at 150°C where ~12% of the adipic acid product decomposes. At this temperature the autoxidation reaction is only 30% selective, consequently, 65% of the reacted cyclohexane is never converted to adipic acid. These calculations are based on the product-distribution data (Table 1) and the decarboxylation data (Table 2) by assuming that the average amount of adipic acid is ½ the final amount and that this average amount decarboxylates to the same extent as the labeled adipic acid.

The yield loss due to decarboxylation at 150°C increased from 1.0 to 3.6% as the
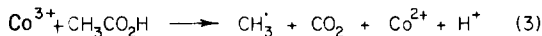
cobalt-catalyst concentration increased from 0.0 to 6.6×10^{-3} M. Based on these results and those of Waters and Clifford (4) and Kochi and Lande (3) it is reasonable to postulate a cobaltic-ion induced decarboxylation. However, since decarboxylation does take place in the absence of a cobalt-catalyst, another mechanism must also be operable—possibly the α-hydrogen abstraction mechanism previously mentioned.

A maximum of 15% of the glutaric acid could be produced by decarboxylation (Table 4). Acetic acid is about 15 times more stable than adipic acid, however because of its relatively high concentration, at 150°C about 30% of the total carbon oxides results from its decomposition into 2 moles of CO$_2$ and/or CO.

While this study has eliminated the decarboxylation mechanism as an important contributor to selectivity loss and glutaric-acid production, it has not established what mechanisms are important. In this regard, it is worth noting that although substantial quantities of CO (35 mmoles) were produced at 150°C (Table 1), the CO contained no radioactivity (Table 2) demonstrating that carbon monoxide is not formed via decarboxylation. It is possible that the CO is the result of the decomposition of acyl radicals produced during the ring opening of cyclohexanone. This is consistent with the high yield of glutaric acid and with the results of Urry and Nicholaides (27) who demonstrated that acyl radicals decompose rapidly [Eq. (2)] at temperatures above 115°C.

$$R-C\overset{O}{\underset{.}{\diagup}} \longrightarrow R\cdot + CO \qquad (2)$$
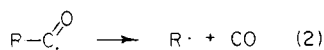
Carbon monoxide might also be produced via the decarboxylation of acetic acid [Eqs. (3) and (4)].

$$Co^{3+} + CH_3CO_2H \longrightarrow CH_3^{\cdot} + CO_2 + Co^{2+} + H^+ \qquad (3)$$

$$2CH_3^{\cdot} + 2O_2 \longrightarrow CO + 3H_2O \qquad (4)$$

A number of previous papers have commented on the catalytic effect of carboxylic acid solvents on autoxidation reactions

TABLE 4

SELECTIVITY-LOSS DUE TO DECARBOXYLATION OF ADIPIC ACID

Oxygen pressure = 50 psia   [Cyclohexanone] = 8.6×10^{-2} M
Moles of O_2 reacted = 0.20   [Co(OAc)$_2$ · 4H$_2$O] = 3.3×10^{-2} M
[Cyclohexane] = 3.3 M   Acetic acid = 9.75 M

| Temp (°C) | Cyclohexane reacted (mmoles) | Adipic acid | | | Selectivity to adipic acid (%) | Selectivity loss due to decarboxylation[b] (%) | Glutaric acid | |
| | | Product (mmoles) | Decarboxylated | | | | | Via decarboxylation[c] |
			(%)[a]	(mmoles)			Observed (mmoles)	(%)
90	77.5 (69.2)[f]	47.7	3.8	0.9	69	1.3	6.4	17
125	51.0 (55.1)[f]	36.2	5.4	1.0	65	1.8	7.5	13
150	36.7 (34.5)[f]	9.9	24.9	1.2	29	3.4	9.2	13
150[d]	67.7 (40.6)[f]	10.2	8.3	0.4	25	1.0	3.0	13
150[e]	32.5 (31.5)[f]	7.8	30.1	1.2	25	3.8	7.1	17

[a] Table 2.

[b] Moles $\left(\dfrac{\text{Adipic decarboxylated}}{\text{Cyclohexane reacted}} \right) \times 100$.

[c] Maximum, if all the decarboxylated adipic acid was converted to glutaric acid.

[d] No catalyst.

[e] Double catalyst, i.e., 6.6×10^{-3} M.

[f] Cyclohexane reacted mmoles minus cyclohexanol and cyclohexanone produced mmoles. Selectivity data concerning acid products are based on these values.

(28, 29). However, attempts to relate the rate acceleration to acidity and polarity changes caused by the addition of carboxylic acids to the system (29) were unsuccessful. It is conceivable that the accelerating effect of carboxylic acids is associated with decarboxylation by transition metal ions either by generating free radicals or by controlling the oxidation state of the metal ion catalyst.

ACKNOWLEDGMENTS

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