Oxidative Decarboxylation of Cyclohexane Monocarboxylic Acid as a Degenerate Branching Chain Reaction II. Mechanism

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Based on the experimental results obtained studying the oxidative decarboxylation of cyclohexane monocarboxylic acid and published earlier, a mechanism is suggested, according to which in the thermal oxidation two main chain carrier radicals exist: tertiary and secondary peroxy radicals yielding cyclohexanone as well as hydroxy and keto acids in parallel reaction sequences. Carbon dioxide is formed in both pathways independently. The corresponding hydroperoxide molecules, formed during oxidation, decompose partly into radicals and partly into molecules resulting in degenerate branching and chemiluminescence phenomena, respectively. The rate determining termination is the cross combination process between secondary and tertiary peroxy radicals. The combinatorial generation of the mechanism of the thermal process and its reduction enabled the construction of the sequence network of the formation of products indicating that the primary attack of the hydrogen

abstraction (secondary or tertiary) determines the product distribution.

Introduction

In Part I [1] we have summarized results on the oxidative decarboxylation of cyclohexane monocarboxylic acid carried out in the absence of catalyst. The practical purpose of the studies was the possibly enhanced production of cyclohexanone.

According to the kinetic approach, it has been established that under the experimental conditions applied, the overall process corresponds to a degenerate chain branching reaction. Based on GCMS measurements, the accumulation of the various products vs. time has been determined at different temperatures, while chemiluminescence results indicated the pathways of the formation of cyclohexanone.

The kinetic treatment of the experimental data yielded the rates of the primary initiation, the rates of the secondary initiation and the rates of the consumption of one of the primary products, cyclohexanone, vs. conversion.

Furthermore, the *rate constant* of the main chain propagation process of the simultaneous formation of cyclohexanone and carbon dioxide has been calculated together with the temperature dependence of the above parameter. In addition, it has been established that with respect to the formation of CO_2 , at least two pathways exist: one results in the accumulation of cyclohexanone, while the other omits this route.

In the present paper, based on these data [1] and literature evidence [2-5] in compiling and handling the corresponding set of elementary processes, a detailed mechanism is assumed describing the experimental observations for the early stages of the overall process.

1. Mechanism of the Oxidative Decarboxylation of Cyclohexane Monocarboxylic Acid in the Initial Period of the Overall Process

Primary Initiation

In contrast to earlier assumptions [6] initiation does not take place by hydrogen abstraction from the carboxyl group, but by the attack of oxygen on the tertiary α -hydrogen. This is supported by the lack of the formation of cyclohexyl hydroperoxide among the products [1]:

$$\bigcirc -\operatorname{COOH} + \operatorname{O}_2 \xrightarrow{k_{i,o}} \bigcirc \bullet \operatorname{COOH}(\alpha) + \operatorname{HO}_2^{\bullet}$$
(1)

Chain Propagations I. (Oxidation of the Substrate)

$$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ &$$

The H-abstraction from the carboxyl group is neglected also in step (3) for the same reason as in reaction (1). Less selective radicals (e.g. 'OH or alkoxy radicals, RO') formed in the overall reaction, as shown later, can attack easily also secondary hydrogen atoms:

•OH +
$$\bigcirc$$
 - COOH $\xrightarrow{k_{4a}}$ H₂O + \bigcirc - COOH(α)
or \bigcirc - COOH(β) (4a)

and

$$\begin{array}{c} & & & & & \\ & & & \\ & & & \\ & + & \\ & - & \\ & & + & \\ & & - & \\ & & + & \\ & & - & \\ & & + & \\ & & - & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$$

Because of the small differences in the strength of β , γ , δ C – H bonds, these types of attack are not distinguishable kinetically and further on notation β refers also for γ , δ hydrogen abstraction. Processes (4a and 4b) are followed by processes (2) and (3) or (5) and (6):

$$\bigcirc -\text{COOH}(\beta) + O_2 \xrightarrow{\text{fast}} \bigcirc -\text{COOH}(\beta)$$
(5)

$$OO^{\bullet} \xrightarrow{k_{p}} OOH \xrightarrow{k_{p}} OOH \xrightarrow{OOH} OOH \xrightarrow{} OOH (\alpha)$$
(6)

Radicals HO_2^{\bullet} formed in process (1) attack also the tertiary hydrogen atom of the substrate:

$$HO_2^{\bullet} + \bigcirc -COOH \xrightarrow{k_{6'}} H_2O_2 + \bigcirc -COOH(\alpha)$$
(6')

It has been assumed [1] that $k'_p = \varepsilon_1 k_p$ where $1 < \varepsilon_1 < 4$, while processes (6) and (6') have closely identical rate constants, that is $k_{6'} \sim k'_p$ [7].

Beside process (3), tertiary peroxy radicals undergo also isomerization:

Thus, according to process (7), cyclohexanone is formed in a chain propagation supported by its amounts accumulated during the oxidation [1]. Namely, if we would assume that it is formed in a radical-radical interaction, which is highly unlikely as it will be seen later, its rate of accumulation would be essentially less than measured.

Chain Propagations II.

(Oxidation of the Intermediate Cyclohexanone)

The oxidation of cyclohexanone has been reviewed in detail in the literature [8-10]. Therefore, here only those steps are referred to, which affect essentially the kinetics and product distribution of the *overall* oxidative decarbox-ylation. Among such reactions, the main chain propagations of the consumption of cyclohexanone are shown. Accordingly, two types of main chain propagations have been suggested: hydrogen abstraction from and addition of peroxy radicals to cyclohexanone:

$$\bigcirc = O + \begin{cases} \bigcirc OO^{\bullet} \\ \bigcirc COOH(\alpha) \\ \bigcirc OO^{\bullet} \\ \bigcirc COOH(\beta) \\ HO_{2}^{\bullet} \\ HO_{2}^{\bullet} \\ \end{pmatrix} \xrightarrow{OOH} \\ \bigcirc OOH \\ OOH \\ \bigcirc OOH \\ OOH \\$$

followed by

$$\overset{\bullet}{\longrightarrow} O + O_2 \xrightarrow{\text{fast}} \overset{OO}{\longrightarrow} O \xrightarrow{\text{substrate}} \overset{OOH}{\longleftarrow} O$$
(9)

Instead of hydrogen abstraction given by (8), both α and β peroxy radicals (RO₂) of the substrate or HO₂ radicals may form an adduct with cyclohexanone:

$$\bigcirc = O + RO_2^{\bullet}(\alpha, \beta) \quad \text{or} \quad HO_2^{\bullet} \longrightarrow$$

$$\bigcirc OOR(\alpha, \beta) \quad OOH \quad OOH \quad (10)$$

followed by:

$$\bigcirc OOR(\alpha, \beta) \\ O^{\bullet} \\ O^{\bullet}$$

At low conversions the role of the keto-peroxy radicals, formed in (9), as *main* chain carriers can be neglected.

Secondary Initiation or Degenerate Branching

In liquid phase oxidation, as a rule, the decomposition of hydroperoxide molecules results in secondary initiation [11]:

$$OOH
COOH(\alpha) \text{ or}
OOH
COOH(\beta) \longrightarrow OH + RO^{\bullet}(\alpha, \beta)$$
(12)

However, according to our chemiluminescence measurements excited triplet cyclohexanone has been formed in a *molecular* process [1] and not in radical-radical interactions as expected. Therefore it has to be assumed that the α hydroperoxide molecules undergo also the following process beside (12) which does not lead to branching:

$$\bigcirc OOH \\ \frown COOH(\alpha) \longrightarrow H_2O + CO_2 + \bigcirc = O \qquad (12a)$$

Thermochemically process (12a) can lead to triplet ketone molecules resulting in chemiluminescence.

Radical-radical interactions and termination

Since in the autoxidation the RO_2^{\bullet} radicals are the main chain carriers and all other radicals (hydroxyl, alkoxy, etc.) are transformed into the former ones, only the interactions of peroxy radicals should be considered.

It is widely accepted, that tertiary peroxy radicals do not undergo Russell-type termination [12, 13], but form oxy radicals and consequently lead to chain propagation:

$$2 \swarrow^{OO^{\bullet}}_{COOH(\alpha)} \longrightarrow 2 \swarrow^{O^{\bullet}}_{COOH+O_2}$$
(13)

The α -oxy radicals react according to (4b) yielding hydroxy-cyclohexane monocarboxylic acid.

At the same time, secondary peroxy radicals lead to stable products in their interactions:

$$2 \bigvee_{-\text{COOH}(\beta)}^{\text{OO}} \longrightarrow 0$$

$$OH \qquad OOH \qquad OOH = OOH + O_2 \qquad (14)$$

The cross combination between tertiary and secondary peroxy radicals also corresponds to a Russell-type reaction:

$$OO^{\bullet} OO^{\bullet} OO^{\bullet}$$

In contrast to (13), both processes (14) and (15) are terminations, although, due to the concentration relations, the rate of the cross combination, (15), exceeds considerably that of combination (13).

Chain Propagations III. (Oxidation of Hydroxy- and Keto-Acids)

Since the kinetic chain lengths of the oxidative decarboxylation of the substrate are relatively small [1] (around 3-5at 140 °C), radical-radical interactions can considerably contribute to the accumulation of hydroxy- and keto-acids, respectively.

Consequently, the oxidation of hydroxy- and keto-cyclohexane monocarboxylic acids, formed in (4b), (14) and (15), proceeds parallel to the oxidation of cyclohexanone and is represented by *overall* processes (16) and (17):

$$\begin{array}{c} OH \\ \hline COOH \xrightarrow{\text{RO}_2^{\circ}(\alpha,\beta) \text{ or } HO_2^{\circ}} \\ \hline O_{2, \text{ substrate}} \end{array} ROOH(H_2O_2) \\ \hline OH \\ + \overbrace{-\text{COOH}} \longrightarrow \text{ products} + CO_2$$
 (16)

$$\begin{array}{c} & O \\ \hline & COOH \xrightarrow{\text{RO}_2^*(\alpha,\beta) \text{ or } HO_2^*} \\ \hline & O_{2, \text{ substrate}} \end{array} \text{ ROOH}(H_2O_2) \\ + \begin{pmatrix} O \\ COOH \\ OOH \end{array} \text{ products} + CO_2$$
(17)

where ROOH corresponds to hydroperoxide derivative of the substrate and "products" do *not* include *cyclohexanone* and are likely to be hydroxy-ketones and di-ketones.

Overall processes (16) - (17) are *important* in order to explain the formation of a part of CO₂ without the *simulta*-



Fig. 1

Scheme of heuristic pathways in the oxidative decarboxylation of cyclohexane monocarboxylic acid. Rad' refers to any radical abstracting hydrogen

neous formation of cyclohexanone as indicated by direct measurements described in Part I. Above assumed ("heuristic") mechanism, suggested for low conversions, can be represented by the scheme of pathways shown in Fig. 1.

Rad[•] stands for *any* radical abstracting hydrogen. Fig. 1 summarizes processes (1) - (17) and indicates the sequence of the formation of stable products and the two main routes in which CO₂ is formed independently.

2. Combinatorial Generation of the Mechanism and the Corresponding Network

Beside the kinetic and "heuristic" approach, attempt has been made to compile the mechanism generated combinatorically according to the computational procedure suggested earlier [14]. This requires the definition of the species participating in the process, separately for the left hand side of the reactions (reactants) and for the right hand side (products). Table 1 lists the set of species, chosen to limit the description of the process to low conversion (until the reactions of products can be neglected, except for the reactions of the hydroperoxides, which provide secondary initiation being already important at early stages).

Table 1

Set of species of the oxidative decarboxylation of cyclohexane monocarboxylic acid

Reactants	Products
Reactants O_2 Substrate $RO_2'(\alpha)$ $RO_2'(\beta)$ $ROOH(\alpha)$ $ROOH(\beta)$ $RO'(\alpha)$ $RO'(\beta)$ H_2O_2 OH HO_2'	Products O_2 Substrate $RO_2^{\prime}(\alpha)$ $RO_2^{\prime}(\beta)$ $ROOH(\alpha)$ $ROOH(\beta)$ $RO^{\prime}(\alpha)$ $RO^{\prime}(\beta)$ H_2O_2 *OH HO_2^{\prime} Hydroxy-acid (α) Hydroxy-acid (β) β -lactone Cyclohexanone H_2O
	$\dot{CO_2}$

Furthermore, it has been assumed, that alkyl radicals react very fast and exclusively with oxygen, consequently these species were not included among the reactants.

All stoichiometrically possible reactions have been generated by computer under conditions that in each elementary reaction the number of reactants does not exceed two and the number of products does not exceed three.

Two characteristic numbers were calculated for each elementary reaction:

 $-\chi$, the number of pairs of atoms, between which there was no bond before the reaction occurred and a new

bond is formed in the reaction, as suggested by Hajdu [15] (this number reflects the geometric constraints of an elementary process),

- standard reaction heats of the elementary processes.

The first reduction of the mechanism generated combinatorically (consisting of 970 stoichiometrically possible reactions) was made with the help of χ : a reaction was considered to be an elementary reaction (i.e. to be retained in the mechanism) if χ does not exceed unity [15] (253 reactions satisfied this condition). The second reduction was made on the basis of thermochemical kinetic treatment as outlined in [11]. As a result 192 reactions remained in the mechanism. Earlier we introduced the concept of the sequence network [14] which shows all precursor-product relations of a given reaction mechanism in a visually easily perceptible manner. It contains only selected species and follows the transformation of any selected atom or group of atoms (thus for the same mechanism many sequence networks can be constructed). Its most important feature is that the existence of an arrow between two species shows that the selected atom (or atomic group) is transfered from one species to the other without being transfered through any other species *included* in the sequence network, whereas the lack of an arrow shows that such a transfer of atom (atomic group) is not realized.

The sequence network of the transformation of the carbon ring of cyclohexane monocarboxylic acid during oxidation is shown in Fig. 2.





Sequence network of the transformation of the carbon ring of cyclohexane monocarboxylic acid during oxidation

As it can be seen from Fig. 2, the primary attack on the substrate plays a decisive role. In case the α -hydrogen is abstracted, α -hydroperoxide, α -hydroxy-carboxylic acid and cyclohexanone can be formed; if the β -hydrogen is abstracted, another series of products is formed. There is *no* cross-communication between the two series of products.

If e.g. production of cyclohexanone is the aim of the decarboxylation this means that *less selective* radicals, which are capable to abstract the β -hydrogen, produce partly undesired products. Since these radicals are formed in the secondary initiation processes (which become the rate-determining initiation steps at very low conversion already), and the chain length of the overall process is rather small, the formation of considerable amounts of undesired by-products cannot be avoided.

This qualitative picture remains unchanged *independent*ly of the actual values of the corresponding (and mostly unknown) rate constants making certain arrows either negligible or rate determining but not resulting in *new* arrows.

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References

- I. Nemes, K. Héberger, Á. Keszler, G. Vasvári, D. Gál, P. Delogu, L. Cotarca, Ber. Bunsenges. Phys. Chem. 98, 75 (1994).
- [2] S.E. Klai, F. Baronnet, J. Chim. Phys. 90, 1951 (1993).
- [3] C. Chevalier, J. Warnatz, H. Melenk, Ber. Bunsenges. Phys. Chem. 94, 1362 (1990).
- [4] G.M. Come, G. Scacchi, C. Muller, P.M. Marquaire, J. Chim. Phys. 85, 201 (1988).
- [5] S. Vajda, P. Valkó, T. Turányi, Int. J. Chem. Kin. 17, 55 (1985).
- [6] I.V. Berezin, A.M. Ragimova, Zh. Fiz. Khim. 36, 581 (1962);
 W.H. Starnes, J. Org. Chem. 31, 1436 (1966).
- [7] J.A. Howard, W.J. Schwalm, K.U. Ingold, Adv. Chem. Ser. 75, 7 (1968).
- [8] I.V. Berezin, E.T. Denisov, N.M. Emanuel, Oxidation of Cyclohexane, Moscow Univ. Press, Moscow 1962 (in Russian).
- [9] E.T. Denisov, N.I. Mitskevich, V.E. Agabekov, Mechanism of the Liquid Phase Oxidation Oxygen-Containing Compounds, Nauka i Technika, Minsk 1975 (in Russian).
- [10] G.E. Zaikov, Kinet. Katal. 9, 1166 (1968).
- [11] N.M. Emanuel, D. Gál, Modelling of Oxidation Processes, Akadémiai Kiadó, Budapest 1986.
- [12] G.A. Russell, J. Am. Chem. Soc. 79, 3872 (1957).
- [13] T.G. Taylor, P.D. Bartlett, Tetrahedron Lett. 24, 30 (1960).
- [14] T. Vidóczy, I.P. Hajdu, I. Nemes, and D. Gál, Ox. Comm. 4, 203-221 (1983); I. Nemes, T. Vidóczy, L. Botár, and D. Gál, Theoret. Chim. Acta 45, 215-224 (1977).
- [15] I.P. Hajdu, unpublished results.
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