Russian Journal of Applied Chemistry, Vol. 76, No. 8, 2003, pp. 1348–1350. Translated from Zhurnal Prikladnoi Khimii, Vol. 76, No. 8, 2003, pp. 1386–1388.

Transformations of Acids in the Course of Ozonolysis of Oxygen-containing Derivatives of Cycloparaffins

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Received March 20, 2003

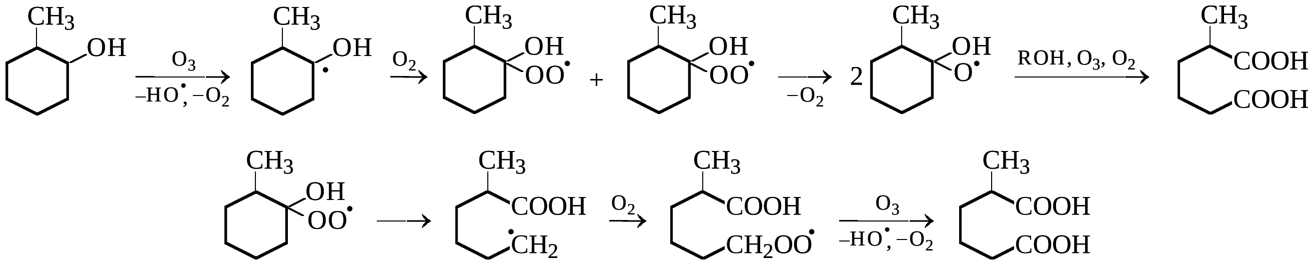
Abstract—Transformations of monocarboxylic, dicarboxylic, and keto acids in the course of low-temperature ozonolysis were studied using the corresponding ^{14}C-labeled compounds.

Deep oxidation of cyclohexane [1], methylcyclohexane [2], and their oxygen-containing derivatives (alcohols, ketones, esters, lactones) [2] results in accumulation of monocarboxylic, dicarboxylic, and keto acids, which are actively oxidized by ozone–oxygen mixtures.

In this study, we analyzed transformations of [2,3-^{14}C]succinic, [2,4-^{14}C]glutaric, [1,2-^{14}C]-α-ketoglutaric, and [1-^{14}C]caproic acids in 2-methylcyclohexanol under conditions of its oxidation at 80°C ($[O_3]$ = 4 vol %).

Procedures for radiochromatographic analysis of the acids are described in [3, 4]. Calculations [2] show that, under these conditions, the hydroxy peroxy radical derived from 2-methylcyclohexanol does not react with the C–H bonds of the acids in hand and of 2-methylcyclohexanol. However, alkyl and alkoxyl radicals and ozone abstract the most labile hydrogen atoms from 2-methylcyclohexanol, labeled acids under consideration, and intermediate oxidation products, including radicals. The radioactive products of ozonolysis of [2,3-^{14}C]succinic acid are [2,3-^{14}C]propionic acid, [2-^{14}C]acetic acid, and $^{14}CO_2$.

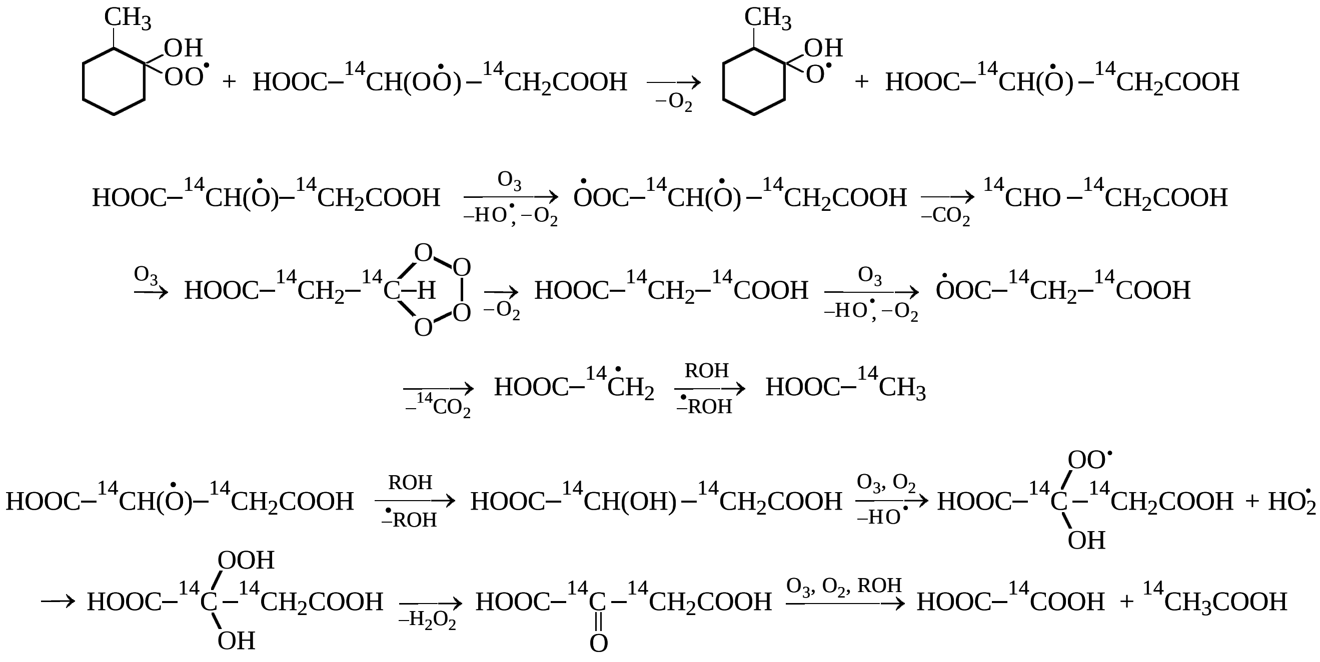
[2,3-^{14}C]Succinic acid is 21.5% decarboxylated in 3 h at 32.5% overall conversion. Ozone attacks the acid at both the methylene chain and the functional group:



$$HOOC{-}^{14}CH_2{-}^{14}CH_2{-}COOH \xrightarrow[-HO^{\bullet},\,-O_2]{O_3} HOOC{-}^{14}CH_2{-}^{14}CH_2{-}COO^{\bullet}$$

$$\xrightarrow[-CO_2]{} HOOC{-}^{14}CH_2{-}^{14}CH_2^{\bullet} \xrightarrow[{}^{\bullet}ROH]{ROH} HOOC{-}^{14}CH_2{-}^{14}CH_3$$

$$HOOC{-}^{14}CH_2{-}^{14}CH_2{-}COOH + O_3 \xrightarrow[-HO^{\bullet},\,-O_2]{} HOOC{-}^{14}\dot{C}H{-}^{14}CH_2{-}COOH \xrightarrow{O_2} HOOC{-}^{14}CH(O\dot{O}){-}^{14}CH_2{-}COOH$$



$$\mathrm{HOOC{-}^{14}CH(\dot{O}){-}^{14}CH_2COOH} \xrightarrow[-\mathrm{H\dot{O}},\,-\mathrm{O_2}]{\mathrm{O_3}} \mathrm{\dot{O}OC{-}^{14}CH(\dot{O}){-}^{14}CH_2COOH} \xrightarrow[-\mathrm{CO_2}]{} \mathrm{^{14}CHO{-}^{14}CH_2COOH}$$

$$\xrightarrow[-^{14}\mathrm{CO_2}]{} \mathrm{HOOC{-}^{14}\dot{C}H_2} \xrightarrow[-{}^{\bullet}\mathrm{ROH}]{\mathrm{ROH}} \mathrm{HOOC{-}^{14}CH_3}$$

$$\mathrm{HOOC{-}^{14}CH(\dot{O}){-}^{14}CH_2COOH} \xrightarrow[-{}^{\bullet}\mathrm{ROH}]{\mathrm{ROH}} \mathrm{HOOC{-}^{14}CH(OH){-}^{14}CH_2COOH} \xrightarrow[-\mathrm{H\dot{O}}]{\mathrm{O_3,\,O_2}} \mathrm{HOOC{-}^{14}C(O\dot{O})(OH){-}^{14}CH_2COOH} + \mathrm{H\dot{O}_2}$$

$$\longrightarrow \mathrm{HOOC{-}^{14}C(OOH)(OH){-}^{14}CH_2COOH} \xrightarrow[-\mathrm{H_2O_2}]{} \mathrm{HOOC{-}^{14}C({=}O){-}^{14}CH_2COOH} \xrightarrow{\mathrm{O_3,\,O_2,\,ROH}} \mathrm{HOOC{-}^{14}COOH} + \mathrm{^{14}CH_3COOH}$$

At 32.5% conversion of [2,3-^{14}C]succinic acid, the total activity of acetic and propionic acids is 10.1%. Hence, the major amount of $^{14}CO_2$ is formed in further ozonolysis of [^{14}C]oxalic acid:

$$\mathrm{HOO^{14}CCOOH} \xrightarrow[-\mathrm{H\dot{O}},\,-\mathrm{O_2}]{\mathrm{O_3}} \mathrm{^{14}CO_2} + \mathrm{H\dot{C}O_2} \xrightarrow[-\mathrm{H\dot{O}},\,-\mathrm{O_2}]{\mathrm{O_3}} \mathrm{CO_2}$$

The probability of recombination of the alkoxyl and hydroxy radicals to form intermediate hydroperoxide is low. However, 2-methylcyclohexanol reacts with ozone to form unstable 1-hydroxy-1-hydrotrioxy-2-methylcyclohexane whose thermolysis generates hydroperoxy radical $\mathrm{H\dot{O}_2}$ [5, 6]. Recombination of the hydroperoxy and peroxy radicals yields α-hydroperoxysuccinic acid. Its decomposition generates the corresponding α-oxyl radical:

$$\mathrm{HOOC{-}^{14}CH(OOH){-}^{14}CH_2COOH}$$
$$\xrightarrow[-\mathrm{H\dot{O}}]{} \mathrm{HOOC{-}^{14}CH(\dot{O}){-}^{14}CH_2COOH}$$

The probability of reaction of this radical with the ozone molecule via O–H bond in the carboxy group is low, since this radical reacts with a high rate constant [7] with alcohol molecules present in excess. However, occurrence of the reaction of the radical with ozone to even a small extent will result in formation of CO_2 by oxidation of the intermediately formed malonic acid:

$$\mathrm{HOO^{14}C{-}^{14}CH_2COOH} \xrightarrow[-\mathrm{H\dot{O}},\,-\mathrm{O_2}]{\mathrm{O_3}} \mathrm{HOO^{14}C{-}^{14}\dot{C}H\,COOH}$$
$$\xrightarrow{\mathrm{O_2}} \mathrm{HOO^{14}C{-}^{14}CH(O\dot{O}){-}COOH}$$
$$\xrightarrow[-\mathrm{H\dot{O}},\,-\mathrm{O_2},\,-\mathrm{CO_2}]{\mathrm{O_3}} \mathrm{\dot{O}O\,\dot{C}H\,COOH} \xrightarrow[-2\mathrm{H\dot{O}},\,-\mathrm{O_2}]{2\mathrm{O_3}} \mathrm{CO_2}$$

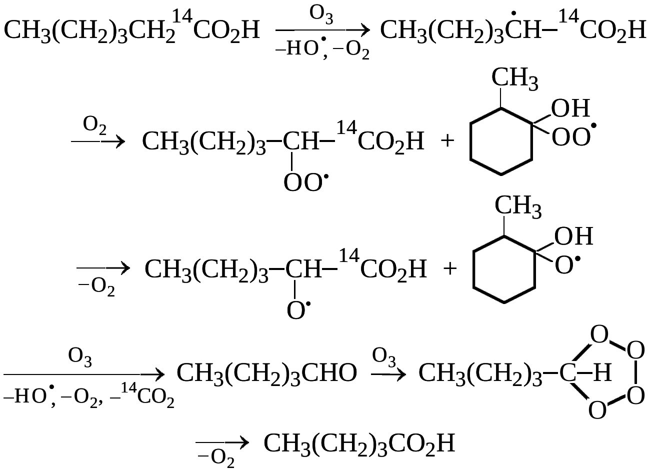
[2,4-^{14}C]Glutaric acid transforms with 30.2% conversion into $^{14}CO_2$ and [2,4-^{14}C]butyric (1.2%), [1,3-^{14}C]succinic (13%), [1-^{14}C]oxalic (0.41%), [1-^{14}C]acetic (0.8%), and [1-^{14}C]propionic (0.45%) acids within 180 min. The composition and activity ratio of the acids show that all the methylene groups of glutaric acid are attacked by ozone. However, the α-methylene groups are attacked predominantly. Note that CH and OH acids can also be attacked by alkoxyl radical.

Under the ozonolysis conditions, [1,2-^{14}C]-α-ketoglutaric acid is 42.5% consumed in 180 min; $^{14}CO_2$ and ^{14}CO are formed in 18.1 and 2.1% yields, respectively. The liquid radioactive products are [1-^{14}C]acetic (0.3%), [1-^{14}C]propionic (1.8%), [1-^{14}C]succinic (13.0%), and [1-^{14}C]oxalic (7.1%) acids. Ozone attacks α-ketoglutaric acid at the α-positions to the carbonyl and carboxy groups and also directly at the O–H bond of the carboxy group. Detection of ^{14}CO shows that ozonolysis involves cleavage of C–C bonds throughout the carbon chain of the keto acid. Experiments with [1-^{14}C]caproic acid showed that it transforms in 180 min with 30.5% conversion into

$^{14}CO_2$, [1-^{14}C]acetic acid (7%), [1-^{14}C]proionic acid (3.5%), [1-^{14}C]butyric acid (3.4%), and small amounts of formic acid:

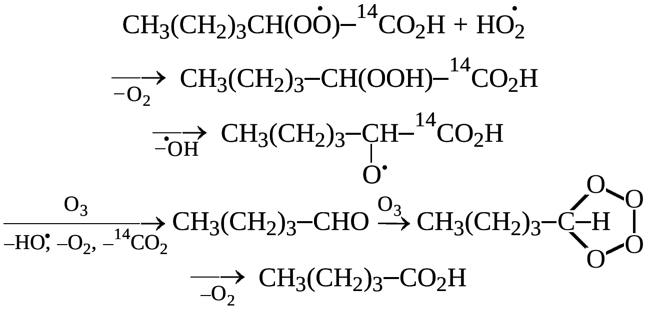
$$CH_3(CH_2)_4{-}{}^{14}CO_2H \xrightarrow[-HO^{\bullet},\,-O_2]{O_3} CH_3(CH_2)_4{}^{14}CO\dot{O}$$

$$\xrightarrow[-^{14}CO_2]{} CH_3(CH_2)_3\dot{C}H_2 \xrightarrow[-\dot{R}OH]{ROH} CH_3(CH_2)_3CH_3$$



By a similar scheme, ozone attacks the remote (β, γ, and δ relative to the carboxy group) methylene groups of caproic acid.

The ratio of the amounts of pentane and valeric acid shows that the probability of ozone attack at the α-position to the carboxy group is 3.6 times higher compared to the attack at the O–H bond of [1-^{14}C]caproic acid. [^{14}C]Formic acid and $^{14}CO_2$ can be formed from the intermediate hydroperoxide by the scheme



$$CH_3(CH_2)_3{-}CH(OOH){-}{}^{14}CO_2H$$

$$\xrightarrow{T,\,O_3,\,ROH} H^{14}COOH + CH_3(CH_2)_3COOH$$

CONCLUSIONS

(1) In ozonolysis (80°C) of [2,3-^{14}C]succinic, [2,4-^{14}C]glutaric, [1,2-^{14}C]-α-ketoglutaric, and [1-^{14}C]-caproic acids, ozone attacks the O–H bond of the carboxy groups and all the methylene groups of the aliphatic chain, predominantly those in the α-position relative to functional groups.

(2) Under the conditions examined, peroxy radicals are inactive in cleavage of the C–H and O–H bonds. The reactions involve ozone, oxygen, and alkyl, alkoxyl, hydroxy, and hyroperoxy radicals.

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