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**ORGANIC SYNTHESIS  
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## Ozonolysis of Methylcyclohexanols and Methylcyclohexanones

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**Abstract**—Ozonolysis of isomeric methylcyclohexanols and methylcyclohexanones was studied.

Oxidation of methylcyclohexane with ozone–oxygen mixtures involves formation of isomeric methylcyclohexanols (MCHLs) and methylcyclohexanones (MCHNs), which subsequently transform into acids and esters. Previously we studied ozonolysis of cyclohexanol [1], cyclohexanone [2], and 1-methylcyclohexanol [3].

Here we consider ozonolysis of secondary alcohols (MCHLs) and the corresponding isomeric MCHNs. The oxidation and analytical procedures are described in [4].

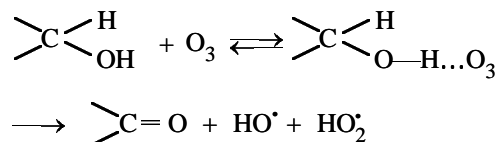
In ozonolysis of methylcyclohexane (MCH), the accumulating secondary and tertiary alcohols are actively consumed. For example, the rate of ozonolysis of 2-methylcyclohexanol grows from  $8.3 \times 10^{-3}$  to  $22.2 \times 10^{-3} \text{ mol l}^{-1} \text{ min}^{-1}$  as the temperature is increased from 40 to 100°C ( $[\text{O}_3] = 4 \text{ vol } \%$ ).

Ozonolysis of secondary MCHLs yields the corresponding isomeric MCHNs (see table), hydroxy hydroperoxides, hydrogen peroxide, esters, and acids [5, 6]. The composition of the acids was studied in detail in [7–9]. The selectivity of ozonolysis of isomeric MCHLs is higher compared to their oxidation with oxygen [6, 10–18]; the yields of the target products are given in the table.

Recombination of hydroperoxy radicals and their reaction with ozone can yield hydroxyalkoxy radicals, which isomerize to form mono- and dicarboxylic acids [19–22]. The acids are also formed by reaction of hydroxy hydroperoxides derived from MCHLs with ozone [6, 15, 16]. The  $\text{RO}^\cdot$  radical is also a source of acids at elevated temperatures. It is formed from the adduct  $2\text{ROH} \cdot \text{H}_2\text{O}_2$  [18] with the activation energy of  $19 \text{ kJ mol}^{-1}$ . In the developed ozonolysis of isomeric MCHLs, the accumulating MCHNs are actively oxidized into acids [20–22] and lactones.

The abnormally high reactivity of ozone toward

nonassociated primary and secondary alcohols [8, 9], along with the reactivity of ozone with alcoholic C–H bonds, discussed in this paper, may also be due to concerted detachment of hydrogen from the alcoholic hydroxy group with ozone [23]:

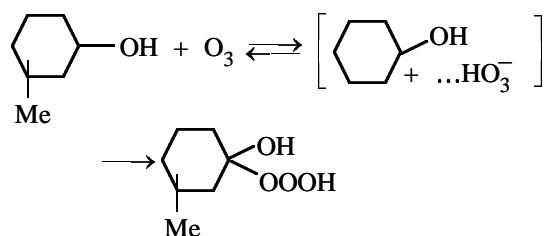


Yield of ozonolysis products of secondary MCHLs\* ( $[\text{O}_3] = 4 \text{ vol } \%$ )

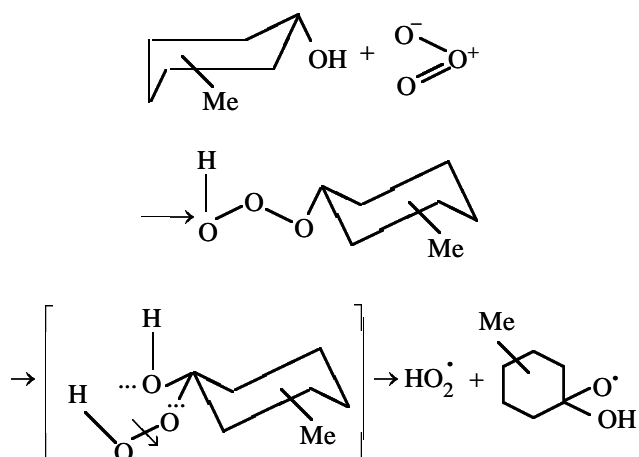
$T, \text{ }^\circ\text{C}$	MCHL conversion, %	Acid content, mol % relative to sum of acids	Yield of MCHN based on converted MCHL, %
4-MCHL			
40	10	80	79
	25	76	75
80	10	79	83
	25	74	73
100	10	83	75
	25	71	72
	50		66
2-MCHL			
40	10	93	
	25	90	
80	10	89	80
	25		75
100	15	88	74
	30	87	63
2-MCHL			
80	10	75	68
	25	72	42

\* Major products: 4-MCHL,  $\beta$ -methyladipic acid and 4-methylcyclohexanone; 2-MCHL,  $\varepsilon$ -ketoanthic acid and 2-methylcyclohexanone; and 3-MCHL, sum of  $\alpha$ - and  $\beta$ -methyladipic acids and 3-methylcyclohexanone.

This reaction is exothermic ( $\Delta H -46 \text{ kJ mol}^{-1}$  [23]) at the C–H bond energy of  $360 \text{ kJ mol}^{-1}$ . Simple hydrogen detachment from the C–H group is endothermic ( $\Delta H 40 \text{ kJ mol}^{-1}$ ). Most probably, ozone reacts with alcohols not only by the radical mechanism discussed above, but also by the mechanism of 1,3-dipolar insertion. The primary molecular product, MCHL hydrotrioxide, can be formed by the mechanism of the hydride ion transfer, with formation of an intermediate ion pair:

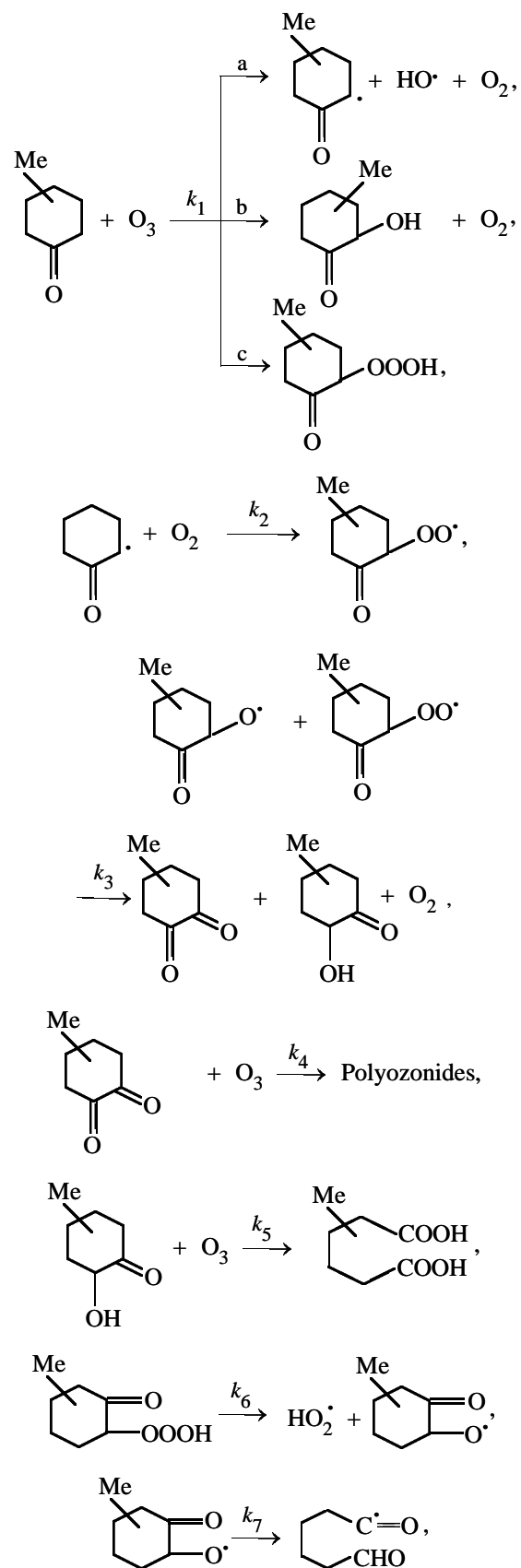


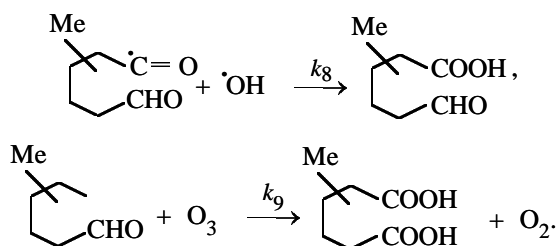
In ozonolysis of methanol, the activation energy of formation of the related ion pair is about  $5 \text{ kJ mol}^{-1}$  [24]. The ionization potential and hence the probability of formation of ion pairs are determined by the structure and concentration of the starting alcohols and by the polarity of the medium. In formation of the intermediate cyclohexanol hydrotrioxide or isomeric secondary MCHLs, the transition state will be stabilized owing to formation of a relatively stable six-membered ring:



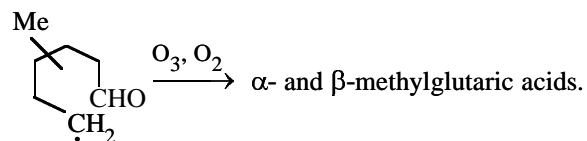
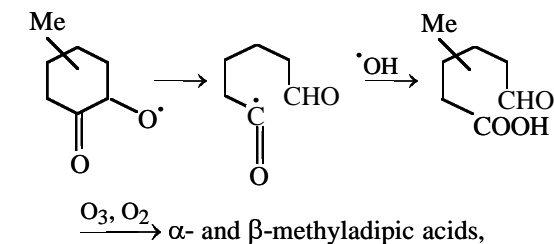
The mechanisms of ozonolysis of cyclohexanone and isomeric MCHLs are similar [2]. The major reaction products are lactones and acids.  $\alpha$ -Keto hydrotrioxide, polyozonides, and isomeric methyl-1-hydroxycyclohexan-2-ones and methyl-1,2-cyclohexanediones are accumulated in smaller amounts.

The mechanism of their formation is schematically shown below:





At lower temperatures (15–20°C), the yield of lactones reaches 52% [25]. As the temperature is elevated (40–80°C), the reaction selectivity with respect to acids grows by 12–16% compared to oxidation with oxygen. Ozonolysis of 4-methylcyclohexanone yields mainly  $\beta$ -methyladipic and  $\beta$ -methylglutaric acids [20–26]. In acidic products of 3-methylcyclohexanone ozonolysis, the major components are  $\alpha$ - and  $\beta$ -methyladipic and  $\alpha$ -methylglutaric acids [6]. In ozonolysis of 2-methylcyclohexanone, the major acidic products are  $\alpha$ -methyladipic,  $\varepsilon$ -ketoanthic, and caproic acids. Formation of acids [15, 21] at elevated temperatures presumably occurs via isomeric  $\alpha$ -keto oxy radicals tending to isomerize with ring opening:



Ozonolysis of MCHNs is more selective than their oxidation with oxygen [14].

## CONCLUSIONS

(1) Ozonolysis of isomeric secondary methylcyclohexanols to the corresponding isomeric methylcyclohexanones is more selective than oxidation with atmospheric oxygen.

(2) Ozonolysis of isomeric methylcyclohexanones mainly yields lactones and acids: monocarboxylic, dicarboxylic, and keto carboxylic.

## REFERENCES

1. Syroezhko, A.M., Proskuryakov, V.A., and Begak, O.Yu., *Zh. Prikl. Khim.*, 2002, vol. 75, no. 9, pp. 1480–1485.

2. Syroezhko, A.M., Begak, O.Yu., and Proskuryakov, V.A., *Zh. Prikl. Khim.*, 2003, vol. 76, no. 5, pp. 814–820.
3. Syroezhko, A.M. and Begak, O.Yu., *Zh. Prikl. Khim.*, 2003, vol. 76, no. 6, pp. 990–995.
4. Korotkova, N.P., Syroezhko, A.M., and Proskuryakov, V.A., *Zh. Prikl. Khim.*, 1981, vol. 54, no. 3, pp. 660–665.
5. Vikhorev, A.A., Syroezhko, A.M., and Proskuryakov, V.A., *Zh. Prikl. Khim.*, 1976, vol. 49, no. 7, pp. 1592–1597.
6. Vikhorev, A.A., Syroezhko, A.M., and Proskuryakov, V.A., *Zh. Prikl. Khim.*, 1976, vol. 49, no. 3, pp. 588–592.
7. Vikhorev, A.A., Syroezhko, A.M., and Proskuryakov, V.A., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1976, vol. 19, no. 10, pp. 1499–1503.
8. Syroezhko, A.M., Korotkova, N.P., Vikhorev, A.A., and Proskuryakov, V.A., *Zh. Prikl. Khim.*, 1978, vol. 51, no. 11, pp. 2562–2567.
9. Syroezhko, A.M., Korotkova, N.P., Vikhorev, A.A., and Proskuryakov, V.A., *Zh. Prikl. Khim.*, 1978, vol. 51, no. 12, pp. 2743–2754.
10. Sukharev, B.N., *Liquid-Phase Oxidation of Isomeric Methylcyclohexanols with Atmospheric Oxygen*, *Cand. Sci. Dissertation*, Leningrad, 1978.
11. USSR Inventor's Certificate no. 555084.
12. Vikhorev, A.A., Syroezhko, A.M., and Proskuryakov, V.A., *Zh. Prikl. Khim.*, 1976, vol. 49, no. 5, pp. 1178–1181.
13. Vikhorev, A.A. and Syroezhko, A.M., in *Issledovaniya v oblasti khimii i tekhnologii produktov pererabotki goryuchikh iskopaemykh* (Studies in the Field of Chemistry and Technology of Products of Fossil Fuel Processing), Leningrad: Leningr. Tekhnol. Inst. im. Lensovetu, 1975, issue 2, pp. 43–45.
14. Serov, V.V., Syroezhko, A.M., Proskuryakov, V.A., and Martynov, Yu.N., *Osn. Org. Sint. Neftekhim.* (Yaroslavl), 1976, no. 5, pp. 9–18.
15. Vikhorev, A.A., Syroezhko, A.M., and Proskuryakov, V.A., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1976, vol. 19, no. 10, pp. 1499–1503.
16. Vikhorev, A.A., Syroezhko, A.M., and Proskuryakov, V.A., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1977, vol. 20, no. 5, pp. 672–676.
17. Vikhorev, A.A., Syroezhko, A.M., and Proskuryakov, V.A., *Zh. Prikl. Khim.*, 1977, vol. 50, no. 6, pp. 1310–1314.
18. Vikhorev, A.A., Syroezhko, A.M., and Yakovlev, A.S., in *Issledovaniya v oblasti khimii i tekhnologii produktov pererabotki goryuchikh iskopaemykh* (Studies in the Field of Chemistry and Technology of Products of

- Fossil Fuel Processing), Leningrad: Leningr. Tekhnol. Inst. im. Lensovet, 1975, issue 2, pp. 39–43.
19. Vikhorev, A.A., Syroezhko, A.M., and Kutuev, R.Kh., in *Issledovaniya v oblasti khimii i tekhnologii produktov pererabotki goryuchikh iskopaemykh* (Studies in the Field of Chemistry and Technology of Products of Fossil Fuel Processing), Leningrad: Leningr. Tekhnol. Inst. im. Lensovet, 1975, issue 2, pp. 38–39.
  20. Vikhorev, A.A., Syroezhko, A.M., and Proskuryakov, V.A., *Zh. Prikl. Khim.*, 1975, vol. 48, no. 9, pp. 2059–2062.
  21. Nonhebel, D.C. and Walton, J.C., *Free-Radical Chemistry. Structure and Mechanism*, Cambridge: Univ. Press, 1974.
  22. Vikhorev, A.A. and Syroezhko, A.M., in *Issledovaniya v oblasti khimii i tekhnologii produktov pererabotki goryuchikh iskopaemykh* (Studies in the Field of Chemistry and Technology of Products of Fossil Fuel Processing), Leningrad: Leningr. Tekhnol. Inst. im. Lensovet, 1975, issue 2, pp. 33–37.
  23. Denisov, E.T., Mechanism of Homolytic Cleavage of Molecules in the Liquid Phase, *Itogi Nauki Tekh., Ser.: Kinet. Katal.*, 1981, vol. 9.
  24. Nangia, P.S. and Benson, S.W., *J. Am. Chem. Soc.*, 1970, vol. 102, no. 9, pp. 3105–3115.
  25. Korotkova, N.P., Syroezhko, A.M., and Proskuryakov, V.A., *Zh. Prikl. Khim.*, 1981, vol. 54, no. 4, pp. 861–867.
  26. Komissarov, V.D., Gerchikov, A.Ya., Galimova, L.G., and Denisov, E.T., *Dokl. Akad. Nauk SSSR*, 1973, vol. 213, no. 4, pp. 881–883.