

On the Application of Oxidative Degradation Reactions in Carboxylic Acid Synthesis

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Oxidation of an ethylenic bond in a hydrocarbon chain involving cleavage and the formation of two carboxyl groups is often used to determine the position of double bonds in unsaturated molecules;¹⁻⁴ if the compound studied is an unsaturated acid, such as oleic acid, the fragments from oxidative cleavage will be a monocarboxylic acid and a dicarboxylic acid. Similarly, cleavage of the chain at the tertiary carbon(s) by strong oxidizing

agents is applied to the determination of the structure of saturated branched-chain fatty acids.^{5,6} For a long time the oxidative cleavage processes have been applied to the production of fatty acids by using mineral oils and paraffins as raw materials,^{7,8} and to make dicarboxylic acids from natural saturated and unsaturated fatty acids.⁹ Different oxidizing agents have been used. Ozone is the preferred oxidant for the directive (or specific) oxidation and cleavage of the ethylenic bond;⁹ whereas the agents most utilized for the random oxidation are oxygen in presence of catalysts at relatively high temperatures,^{7,9} chromic acid, and nitric acid.⁹

It is well known that the oxidizing power of permanganate ions depends on the pH of the medium, and increases in order neutral < alkaline < acid.^{10,11} It has been suggested as a general rule that

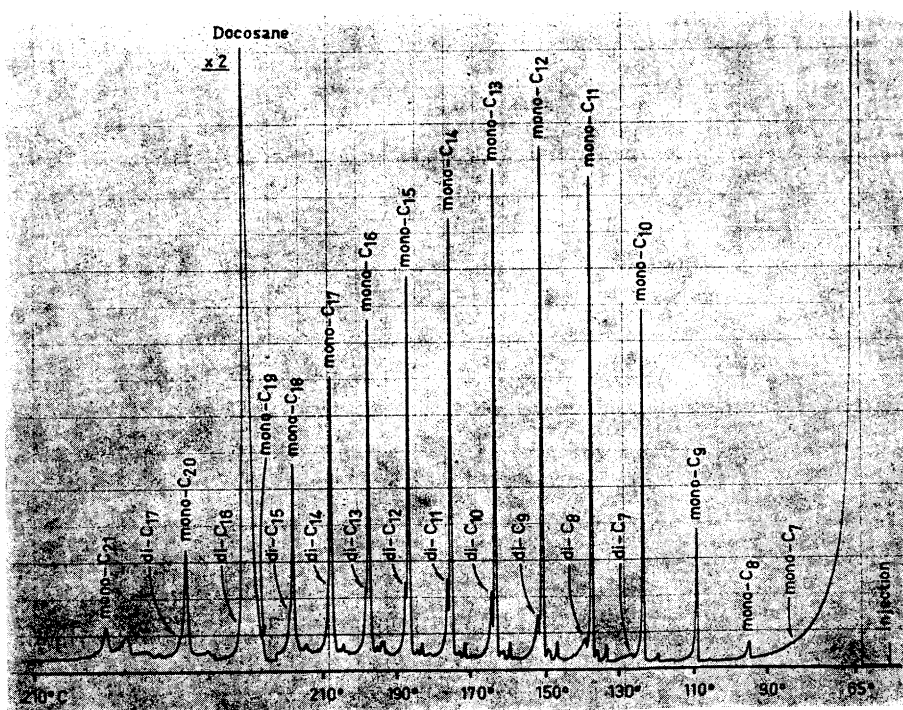
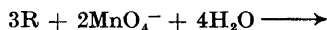


Fig. 1. Gas-liquid chromatogram of the methyl esters prepared from acids formed by permanganate oxidation of docosane. The positions of the esters of monoacids and diacids are marked. The unchanged hydrocarbon is about 20%. Conditions: glass capillary column (length 20.5 m, diameter 0.39 mm) coated with silicone GE SE-30; nitrogen pressure 4 p.s.i.; flame ionization detector; temperature programmed from 65° to 210° at a rate of 4°C/min.

saturated carboxylic acids are not attacked by permanganate ions owing to the stability of the C—H and C—C links of paraffin chains.¹² This suggestion seems to be right in certain circumstances but can not be considered as a general rule, since the saturated normal long-chain fatty methyl esters, which are slightly attacked by permanganate in boiling acetone, are extensively oxidized and degraded by this agent in warm acetic acid giving rise to whole homologous series of mono- and dicarboxylic acids.^{13,14}

Thus, in the acetic acid medium the permanganate is a powerful oxidant for the degradation of paraffin chains. This extensive oxidative degradation has been exploited and applied to the location of deuterium in the partly deuteriated methyl esters¹⁴ and to the synthesis of saturated mono- and dicarboxylic acids using starting products such as fatty acids or corresponding esters, glycerides, bee wax, long-chain alcohols or hydrocarbons, and paraffins (of low m.p.).¹⁵ Fig. 1 shows the gas-liquid chromatogram of a mixture composed of methyl monocarboxylates and dimethyl dicarboxylates derived from the corresponding acids formed through permanganate oxidation of a hydrocarbon.

This process is useful in preparative work on organic deuterium compounds, since with a starting perdeuteriated long-chain fatty acid or hydrocarbon, which may be prepared by a convenient method early described,¹⁵⁻¹⁷ one can obtain a whole homologous series of perdeuteriated mono- and dicarboxylic acids. As has been shown in an earlier report,¹⁸ basic ions are able to catalyse the exchange of deuterium belonging to the alkyl chain of acids for hydrogen of polar solvents; thus the presence of HO⁻ in the reaction medium, according to the permanganate oxidation of an alkyl chain



could cause the loss of the heavy isotope. However, thanks to the use of acetic acid as solvent, which is able to neutralize the basic ions, the hydrogen-deuterium exchange could be avoided.

Details of the present oxidative degradation process will be published later.

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1. Keppler, J. G. *Rec. Trav. Chim.* **76** (1957) 49.
2. Cordier, P. *Mises au point Chim. anal. pure et appl. et Anal. bromatol.* **7** (1959) 33.
3. Privett, O. S. In Holman, R. T. *Progress in the chemistry of fats and other lipids*, Pergamon, Oxford—London—New York 1966, Vol. 9, part 1, chap. 3.
4. Jones, E. P. and Davison, V. L. *J. Am. Oil Chem. Soc.* **42** (1965) 121.
5. Cason, J. and Fessenden, J. F. *Science* **128** (1958) 1143.
6. Murray, K. E. *Australian J. Chem.* **12** (1959) 657; **15** (1962) 510.
7. Cf. Grimberg, M. *Seifen-Oele-Fette-Wachse* **90** (1964) 478.
8. Cf. Zilch, K. T. *J. Am. Oil Chem. Soc.* **45** (1968) 11.
9. Cf. Logan, R. T. In Pattison, E. S. *Industrial fatty acids and their applications*, Reinhold, New York 1959, chap. 5.
10. Cf. Kirk, R. E. and Othmer, D. F. *Encyclopedia of chemical technology*, Wiley, New York 1967, Vol. 14, p. 175.
11. Stewart, R. In Wiberg, K. B. *Oxidation in organic chemistry*, Academic, New York and London 1965, Part A, p. 35.
12. Turney, T. A. *Oxidation mechanism*, Butterworths, London 1965, p. 119.
13. Dinh-Nguyễn, Ng. and Raal, A. *Swed. Pat. Appl.* **16,972** (1968).
14. Dinh-Nguyễn, Ng. and Raal, A. *To be published*.
15. Dinh-Nguyễn, Ng. and Stenhagen, E. *Swed. Pat. Appl.* **1,280** (1965).
16. Dinh-Nguyễn, Ng. and Stenhagen, E. *Acta Chem. Scand.* **20** (1966) 1423.
17. Dinh-Nguyễn, Ng. and Stenhagen, E. *To be published*.
18. Dinh-Nguyễn, Ng. *Acta Chem. Scand.* **16** (1962) 2301.

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