

The Formation of Potassium Perchlorate from Potassium Chlorate.—

The action of certain of the stronger acids on potassium chlorate is not commonly considered as a method applicable to the preparation, in the laboratory, of potassium perchlorate. The action of sulfuric acid on potassium chlorate with the formation of the perchlorate was first recorded by Stadion.¹ Later, Penny² noted that nitric acid acting on the chlorates of potash and soda yielded perchlorate; and shortly after, Millon³ speaks of the formation of the perchlorate by the action of sulfuric acid on the chlorate.

While the action of strong sulfuric acid on potassium chlorate, yields as it does at first, perchlorate and the oxides of chlorine, consisting largely of the tetroxide, the explosive character of the reaction is such that it is very difficult to control. It can, however, be carried out without danger by adding the sulfuric acid slowly and avoiding warming. Decomposition is complete in about 5 hours and is shown by the disappearance of the yellow color accompanying the decomposition of the chlorate. When 2 to 5 g. of chlorate is treated with 50 cc. of conc. sulfuric acid, the yield of perchlorate is about 11%.

Nitric acid of various degrees of concentration will convert potassium chlorate to the perchlorate. A good procedure consists in repeated evaporations to dryness of the chlorate on the steam-bath with ordinary conc. nitric acid. The final product is only the nitrate and perchlorate the yield being as high as 30%. Anhydrous nitric acid gives with potassium chlorate just about the same amount of the perchlorate when evaporated on the steam-bath as does ordinary concentrated acid. Fuming nitric acid, doubtless on account of the reducing character of the acids of nitrogen contained, yields almost no perchlorate.

Phosphoric acid with chlorate yields perchlorate. When the chlorate is boiled with 85% phosphoric acid until the disappearance of the yellow chlorine color, a yield of as high as 15% of perchlorate is obtained.

Chromium trioxide and chlorate, boiled with just enough water to keep the mixture in solution, afford a yield of about 11% of perchlorate.

When chloric acid in a concentration of 30% is allowed to stand for several days in contact with potassium chlorate, then warmed and evaporated with hydrochloric acid in order to destroy all chloric acid and chlorate, no perchlorate is obtained.

Certain acids do not decompose the chlorate, even at the boiling temperature. Among these may be mentioned saturated oxalic acid solution, 25% tartaric acid, acetic acid both glacial and dilute, 50% monochloroacetic, 25% lactic, 50% arsenic, 20% permanganic and persulfuric acid. Other acids, such as formic, trichloro-acetic, hydrofluoric, and hydrochloric acids decompose the chlorate but without yielding perchlorate.

¹ Stadion, *Gilbert's Ann.*, 52, 197 (1818).

² Penny, *Brit. Assoc. Rep.*, 1840, 79.

³ Millon, *Ann. Chem.*, [3] 7, (1843).

Reference to the hydrogen-ion concentration of these various acids gives no apparent reason for the behavior of the various acids. A view to be considered is that the action is selective and follows along the same lines as that of heating the chlorate alone, when rearrangement takes place, 3 molecules of the chlorate being oxidized at the expense of another molecule. In the cases of the action of certain acids on the chlorate, we have the same general character of reaction going on, only at lower temperatures than when the chlorate is heated alone.

MADISON, WISCONSIN.
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VICTOR LENHER,
HOSMER W. STONE
AND HELEN H. SKINNER.

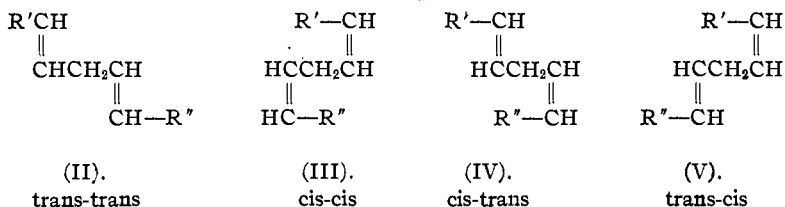
[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

C₁₈ ACIDS. III. FOUR TETRAHYDROXY-STEARIC ACIDS DERIVED FROM LINOLIC ACID, AND THEIR SIGNIFICANCE WITH REGARD TO THE LINOLIC ACID OF COMMON OILS.

BY BEN H. NICOLET AND HENRY L. COX.¹

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In spite of the relatively considerable amount of work that has been done on linolic acid, C₁₈H₃₂O₂, our knowledge of its chemistry is rather strikingly limited. There is a moderate amount of evidence² that its formula is represented by (I) CH₃(CH₂)₄CH=CHCH₂CH=CH(CH₂)₇CO₂H. Four space isomers of such a substance are possible.



in which R' represents the radical CH₃(CH₂)₄— and R'' represents (CH₂)₇CO₂H. No attention has apparently been paid to the question of which, or how many of these occur in natural glycerides, except for Bedford's³ suggestion that there are two different acids of this formula, because the addition of bromine yielded two tetrabromides. Takahashi⁴ has shown further that the α-tetrabromide (m. p. 114°) of linolic acid, when treated with zinc under proper conditions for the elimination of bromine, gives a linolic acid which, on re-bromination, yields two or more tetrabromides (two crystalline products, and an oil which may or may not have been a mixture of these). Each of these products, on removal of bromine, re-

¹ The material here presented is used by Henry L. Cox in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

² Goldsobel, *Chem. Ztg.*, 1906, 825.

³ Bedford, *Dissertation*, Halle a. S., 1908.

⁴ Takahashi, *J. Tokyo Chem. Soc.*, 40, 233-89 (1919); *C. A.*, 13, 1583 (1919).