

absorbed by rubber. In fact, rubber tubing will completely remove mustard from an air stream, only to give it off later when the tube is more or less saturated.

The easiest way to obtain a given partial pressure of mustard in an air stream is probably to make a saturator by taking a U-tube, inserting a folded filter paper in each arm in such

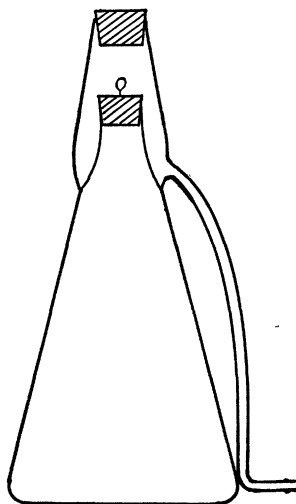


Fig. 1

a way as to give a large surface, and then pouring in enough mustard to dampen the filter paper by capillary rise. This U-tube can then be put in a beaker of water of any desired temperature below room temperature to give the desired partial pressure. We have recently submitted to the *Journal of the American Chemical Society* an article giving vapor pressure data on mustard which fit the equation $\log_{10} p = 9.4819 - 3117.2/(t + 273.1)$, in which p is the vapor pressure in millimeters and t is the centigrade temperature.

Oxidation of β -Carotene With Osmium Tetroxide

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The successful oxidation of carotene at the central double bond to form vitamin A aldehyde, accomplished by Hunter and Williams (3) using hydrogen peroxide, indicated that a catalyst was necessary to improve their low yield (0.5 per cent). Osmium tetroxide, used by Criegee (1) for the oxidation of anethole and other ethylenic compounds, seemed to have the characteristics of being such a substance, since, with hydrogen peroxide, both aldehydes and glycols are formed (4).

If one of the central double bonds can be formed into the epoxide simultaneously with formation of a diglycol at the other, then the resulting compound is identical with the postulated intermediate of the Cannizzaro reaction. This, according to Fredenhagen and Bonhoeffer (2), undergoes rearrangement prior to fission, which would account for β -carotene having half the biological value of vitamin A by weight, and corresponding lower values for other provitamin A compounds.

In applying the reaction of Criegee it has been found that a 1 per cent ethereal solution of osmium tetroxide cannot be prepared from the solid and kept, as it is all reduced in a few hours. An aqueous solution has therefore been employed. Similarly, 30 per cent hydrogen peroxide (aqueous) has been used, although in both cases the reaction proceeds faster with a slightly higher yield if the solutions used are anhydrous in the initial stages.

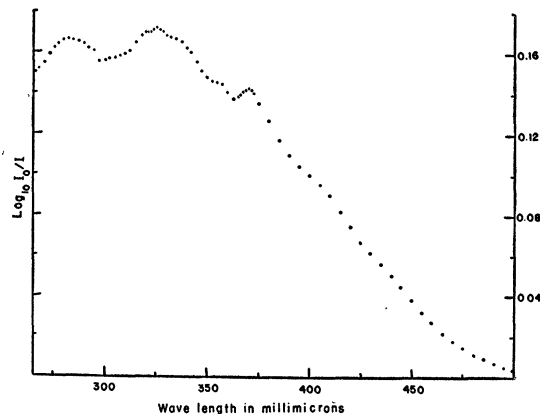


Fig. 1. Absorption curve of oxidation products of β -carotene in cyclohexane.

This work is still in progress, and the details will be published at a later date. However, a typical set of conditions for the reaction is as follows:

About 10 grams of anhydrous sodium sulfate is introduced into a 500-ml., three-necked flask fitted with a reflux condenser, a sealed stirrer, and a burette. For the initial stages the reflux condenser should be fitted with a loosely packed, calcium chloride drying tube. A 50-ml. aliquot of a solution of carotene (90 per cent β - and 10 per cent α -carotene) in anhydrous, alcohol-free ethyl ether is run in from the burette, followed by 1 ml. of a 2 per cent aqueous solution of osmium tetroxide, the solution is stirred for 5 minutes or until a color change is observed, and 2 ml. of 30 per cent hydrogen peroxide is then introduced dropwise. The solution is stirred for 10 minutes, 3 ml. of a 0.5M sodium bicarbonate solution is added slowly, and the stirring is continued until there is no further effervescence. A mixture of 50 ml. of 95 per cent ethyl alcohol and 5 ml. of 50 per cent potassium hydroxide solution is added. The solution is stirred for a further 10 minutes, then decanted into a 500-ml. separatory funnel, and 50 ml. of ethyl ether is added. The funnel is then shaken thoroughly, the lower layer run off, and the supernatant washed as in vitamin A analysis.

An aliquot of the resulting solution is dried over anhydrous sodium sulfate, evaporated under reduced pressure, and taken up in cyclohexane. The absorption spectrum of this solution shows maxima at 283, 325, and 370 $m\mu$ (Fig. 1). If the intensity of the blue color with antimony trichloride, measured at 620 $m\mu$, is due to vitamin A, the yield is 30–40 per cent of the theoretical conversion of β -carotene to vitamin A.

References

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