at 25 mm. pressure is collected. The yield of distilled ester averages about 85%.

CONTRIBUTION FROM THE
DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
SCHOOL OF MEDICINE
LOS ANGELES, CALIFORNIA

PAUL W. JEWEL
JOSEPH S. BUTTS

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COMMUNICATIONS TO THE EDITOR

THE BROMINE-SENSITIZED OXIDATION OF UNSATURATED HYDROCARBONS

Sir:

If one absorbs a pure unsaturated hydrocarbon (C_2H_4, C_3H_6 or C_4H_8) in the presence of pure oxygen by means of bromine water, more gas is absorbed than corresponds to the hydrocarbon present. This extra decrease in volume is not accounted for by the solubility of oxygen in bromine water, for the same results were obtained when the bromine water was presaturated with oxygen.

Thus a bromine-sensitized formation of carbon dioxide and water, both of which would be dissolved in aqueous solution, was suspected. In order to test this assumption in a simple experiment, one side of a 300-cc. sphere was connected to a high vacuum pump through a stopcock and a liquid air trap, the other side communicated, through an ordinary stopcock, a capillary, and a three-way stopcock, with a mercury manometer and a mercury Toepler pump. A tube containing some bromine was also attached to the bulb. The two stopcocks adjacent to the sphere were lubricated with Stephens' stopcock grease [H. N. Stephens, THIS JOURNAL, **52**, 635 (1930)]. The system was evacuated, the bromine evaporated and frozen out again with liquid air. The procedure was repeated and the sphere filled with bromine corresponding to its vapor pressure at about 30° (about 100 cc., N. T. P.). The bromine tube and the pumping line were sealed off between sphere and stopcock. The bromine was again frozen out and a mixture of specially purified ethylene (56.7 cc., N. T. P.) and oxygen (55.2 cc.) was filled in on top of the frozen bromine. The manometer was then opened and read. The two stopcocks were closed, leaving some oxygen in the manometer, and the capillary between the stopcocks was cut in two. The sphere was exposed to direct sunlight, then the liquid air removed and the sphere gently rotated[1] to distribute the bromine. The bromination took place immediately. After two hours of exposure the sphere was immersed to exactly the same point in liquid air and again sealed on the system. The

[1] This seemed to be of great importance.

gas pressure was less than before, showing that some oxygen had disappeared. The oxygen was pumped off; less was recovered than was put in (53.1 cc.) [analysis according to Franzen, *Ber.*, **39,** 2069 (1906)]. The sphere was then heated to $-79°$, whereupon the pressure increased. Some gas was pumped off and analyzed with barium hydroxide for carbon dioxide. The precipitate showed the presence of carbon dioxide (1.4 cc.).

The new effect may be considered analogous to the chlor-sensitized carbon-dioxide formation from carbon monoxide which has been studied by Bodenstein and co-workers. The effect is in interesting contrast to that reported in a brief note recently published by R. Livingston [*J. Phys. Chem.*, **34,** 2121 (1930)]. If his data are correct, one must assume that carbo-oxides (CO) are not oxidized in a bromine-sensitized reaction, whereas carbo-hydrides (C_2H_4) are oxidized to a slight extent. An energy chain propagated by the heat of formation of the water formed may account for this difference. Incidentally, the bromination of the hydrocarbon and its heat effects must be taken into account.

The bearing of this new type of reaction upon the use of the bromine pipet will be reported in a paper soon to appear.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA
GEORG R. SCHULTZE

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THE ALLEGED SELENIUM TRIOXIDE OF WORSLEY AND BAKER

Sir:

The method reported by Worsley and Baker[1] for the preparation of selenium trioxide has failed to yield that substance when carried out by Meyer and Pawletta,[2] and more recently Hoffman and Lenher[3] have shown that the product is selenium dioxide contaminated with water and selenium oxychloride.

In 1927–1928 the Worsley and Baker experiment was repeated in this Laboratory. Selenium oxychloride was prepared by the dehydration of selenium hydroxychloride[4] and redistilled twice under diminished pressure. This material melted at 9.4° and showed also by the test with cobalt carbonate[5] that it contained traces of water. Highly purified selenium was dissolved in this solvent and oxidized with ozone (18 g. of O_3 per cu. meter of O_2). The precipitate obtained after thirty hours was examined. It contained traces of chlorides which could not be removed

[1] Worsley and Baker, *J. Chem. Soc.*, **123,** 2870 (1923).
[2] Meyer and Pawletta, *Ber.*, **60,** 985 (1927).
[3] Hoffman and Lenher, THIS JOURNAL, **51,** 3177 (1929).
[4] Muehlberger and Lenher, *ibid.*, **47,** 1842 (1925).
[5] Lenher, *ibid.*, **43,** 32 (1921).