obtain a ratio between the quantity of gases removed at different temperatures. As is invariably the case with liquids that tend to separate into two components, the less volatile one of the two (the ethane) was easier to obtain in a pure state. It is intended to repeat the work with a smaller percentage of one of the gases present than of the other and with the use of a thermostat such as was devised by F. Henning.[1] In another communication will also be shown the application of this method of separation to substances that are liquids at ordinary temperatures. In some separations the advantages over the use of high temperatures are: (1) The elimination of complicated still heads, and (2) the avoidance of loss by evaporation because high temperatures are not used. A different means of trapping the liquid had to be devised than that used in handling liquid gases.

All temperatures are in degrees centigrade. Details of the apparatus used are given in previous communications.

PITTSBURGH, PA.

[FROM THE CHEMICAL LABORATORY OF THE COLORADO AGRICULTURAL COLLEGE.]

ON THE OXIDATION OF ETHER.

BY R. M. ISHAM AND C. E. VAIL.

Received February 5, 1915.

It seems somewhat surprising to the authors that the subject of the oxidation of ether should have received but slight attention from the writers of our texts on organic chemistry. While the behavior of the alcohols and aldehydes on oxidation is considered in some detail, as representing important type reactions of these substances, the majority of our texts have nothing at all to say regarding the behavior of the closely related ethers. This is the more remarkable in consideration of the fact, which we shall show, that ether is very readily oxidized to aldehyde and acetic acid.

In the third American edition of Richter's "Organic Chemistry," Vol. I, p. 133, we find the statement that "When oxidized they (the ethers) yield the same products as their alcohols." Stoddard's "Introduction to Organic Chemistry," p. 73, states that "Oxidation (of ether) by means of nitric or chromic acid produces the same products as those obtained by the oxidation of alcohol—aldehyde and acetic acid." On the other hand, the 1907 edition of Roscoe and Schorlemmer's "Treatise on Chemistry," Vol. II, p. 1002, states that "Chromium trioxide dissolves without alteration......in pure ether," a statement which we were by no means able to verify. Aside from the above we have not, in a neces-

---

[1] *Z. Instrumentenkunde*, 33, 33 (1913). This thermostat was installed by the authors just before this article went to press. With it temperatures can be controlled within 0.03°.

sarily somewhat incomplete survey of the texts, found any reference to this subject.

Löw[1] has shown that ether vapor, when mixed with air and passed over a heated superficially oxidized copper spiral, is oxidized to aldehyde.

W. H. Perkin[2] found that when ether vapor mixed with oxygen, in a quantity insufficient to produce total oxidation, was passed through a tube heated to temperatures between 260° and dull redness, a pale luminous flame resulted, and the ether was oxidized, chiefly to aldehyde. Similarly, Dunstan and Dymond[3] found the incomplete *combustion* of ether to give aldehyde and acetic acid as chief products.

Richardson and Forty[4] obtained evidence of a photochemical oxidation to aldehyde and acetic acid, on exposing a vessel containing ether and oxygen, in contact with water, to direct sunlight for a period of five weeks.

Aside from the above we have been able to find no reference to the direct oxidation of ether by means of air or oxygen.

We have been able to show that ether vapor is readily oxidized to aldehyde and acetic acid, when mixed with air or oxygen, without the use of any catalyst and at temperatures very much below that at which luminous combustion begins.

The attention of one of us was first directed to this subject when a strong odor of acetaldehyde was noted issuing from a Freas electric oven, in which the residues from the ether extraction of some wheat samples were being dried at a temperature of 110°. The natural inference that the aldehyde resulted from the oxidation of ether was shown to be correct by saturating some filter papers with ether and placing them in the oven, when, after heating for some time at 110°, a strong odor of aldehyde was noted on opening the oven. Since the literature on this subject seemed to be somewhat incomplete we were lead to carry out some further experiments.

A three-holed Woulff bottle of 750 cc. capacity was fitted with an inlet tube extending to the bottom of the bottle, an exit tube extending only through the stopper, and a thermometer, and the whole placed in an air bath.

In a preliminary experiment a side-neck test tube, containing 10 cc. of pure ether, and provided with an inlet tube for oxygen, extending to the bottom, was connected to the inlet tube of the Woulff bottle, and a Liebig condenser attached to its exit tube. The temperature of the Woulff bottle was brought to 120°, while the temperature of the ether was maintained at 12° ± 1, at which temperature, and at our normal barometric

---

[1] *J. prakt. Chem.*, **141**, 323.

[2] *J. Chem. Soc.*, **41**, 363 (1882).

[3] *Ibid.*, **57**, 574 (1890).

[4] *Ibid.*, **69**, 1352 (1896).

pressure (ca. 635 mm.), a mixture of its saturated vapor with oxygen should be nearly equimolecular, as required for the equation:

$$(C_2H_5)_2O + O_2 = 2CH_3CHO + H_2O$$

Oxygen was bubbled through the ether at such a rate that evaporation was complete in a little less than two hours, so that the mixed gases were exposed to the elevated temperature of the Woulff bottle for an average period of about ten minutes. A very strong odor of aldehyde was apparent in the vapors issuing from the condenser, and a couple of drops of the condensed product, which consisted largely of ether, immediately restored the color to a little Schiff fuchsin-aldehyde reagent.

The formation of aldehyde having thus been proven, it was decided to so modify our apparatus as to permit of quantitative experiments. For this purpose, the condenser was replaced by a thistle-tube, connected to the exit tube of the Woulff bottle, and extending to the bottom of a cylinder which contained a little strong ammonia water, and was surrounded by a freezing mixture of snow and salt.

In our first experiment with the modified apparatus the temperature of the Woulff bottle was maintained at 132° ± 2, and that of the ether at 12° ± 1. 10 g. of ether were taken, and oxygen was bubbled through at such a rate that evaporation was complete in an hour and forty minutes. Assuming that the oxygen was saturated with ether vapor, the average time of exposure of the mixture to the elevated temperature was approximately ten minutes. The passage of oxygen was continued until all ether and aldehyde vapor had been swept out of the Woulff bottle. The thistle-tube was then disconnected and rinsed down into the cylinder, the contents of which consisted of an aqueous ammoniacal layer and an ether layer. These liquids were then transferred to an Erlenmeyer flask. No attempt was made to distinguish between the amount of ether which had been oxidized to aldehyde, and that which had been oxidized to acetic acid, but the total amount oxidized was determined as follows, using a modification of the method of Blank and Finkenbeiner:[1] 50 cc. of pure hydrogen peroxide and 50 cc. 0.5 N sodium hydroxide solution were added. The solution was warmed until oxidation of the aldehyde was complete and the excess of peroxide decomposed, then boiled until the last trace of ammonia was expelled. It was then cooled, the sides of the flask rinsed down, and the excess of sodium hydroxide titrated with 0.5 N sulfuric acid, using litmus as indicator. 43.3 cc. of acid were required, showing that 6.7 cc. of 0.5 N sodium hydroxide, equivalent to 0.47 g. of acetic acid or 0.29 g. ether, had been neutralized by the oxidation products. Hence the ether was oxidized to the extent of 2.9%.

In another experiment all conditions were maintained the same, except that a bypass for oxygen was installed, so that approximately double

---

[1] *Ber.*, 31, 2979 (1898).

molecular quantities of oxygen acted on the ether vapor, and the time of the experiment was prolonged to eight hours, whereby the time of exposure of the gas mixture to the elevated temperature was considerably lengthened. We were very much surprised, on titration of our product, to find that the extent of oxidation was identical with that obtained in the former experiment, namely, 2.9%, a coincidence which we do not attempt to explain.

In an effort to obtain a more complete oxidation of the ether we further modified our apparatus by dispensing with the bypass for oxygen and introducing a Woulff bottle of 1400 cc. capacity in place of the smaller one. In our later experiments we maintained the temperature in the Woulff bottle at 160°. Three experiments were carried out under these conditions. In the last of these we determined on one aliquot portion of the distillate the total percentage of ether oxidized, according to the method given above, and on another aliquot the percentage oxidized to acetic acid. This last determination was made as follows: The distillate, collected as before in a cylinder containing strong aqueous ammonia, surrounded by a freezing mixture, was made up to 500 cc. and an aliquot portion of 100 cc. taken. 50 cc. of 0.5 *N* sodium hydroxide solution were added and the solution boiled until ammonia and aldehyde were expelled. A slight resinification of the aldehyde was indicated by the fact that the solution became yellow as the boiling proceeded. After all ammonia was expelled, the solution was cooled and the excess of alkali titrated with 0.5 *N* sulfuric acid, using litmus indicator. The results of the three experiments are summarized in the appended table:

Expt. No.	Grams ether taken.	Duration of expt. Min.	Ave. time of exposure to 160° temp.	% ether oxidized		
				to ald.	to acid.	total.
1................	10	160	35	..	..	32.5
2................	5	70	30	..	..	35.2
3................	5	70	30	11.6	23.9	35.5

As may be seen from the results of the third experiment, the major part of the aldehyde produced was further oxidized to acetic acid. Since the ether vapor and oxygen were originally present in equimolecular proportions as required for the equation

$$(C_2H_5)_2O + O_2 = 2CH_3CHO + H_2O$$

it will be seen that there was only enough oxygen present to convert one-half of the ether to acetic acid according to the equation

$$(C_2H_5)_2O + 2O_2 = 2CH_3COOH + H_2O.$$

From the results of this experiment we see that 2 × 23.9 + 11.6 or 59.4% of the oxygen was used in oxidizing 35.5% of the ether. This result would indicate that the introduction of more oxygen was essential to secure complete oxidation of the ether. When, however, we attempted to carry out experiments using a larger proportion of oxygen, we found that even with initial temperatures as low as 150° the reaction was so rapid that the gas mixture was subject to sudden rises in temperature and subsequent explosions. Consequently we were obliged to abandon the attempt to show that ether can be quantitatively oxidized under these conditions.

In an effort to check the apparent contradiction in the literature on the effect of chromic anhydride on ether, some pure chromic anhydride was prepared, and added to pure ether. A very violent reaction, with evolution of aldehyde vapors, and separation of green chromic oxide, resulted. When the ether was cooled in a freezing mixture to —10° and the chromic anhydride added, a yellow solution was momentarily produced, but reaction began almost at once with the same results as before.

Summary.

1. Ether vapor is oxidized to aldehyde and acetic acid, when heated with air or oxygen.

2. This oxidation begins at temperatures as low as 110°, and is very rapid at 160°.

3. Chromic anhydride does not dissolve without alteration in pure ether.

FORT COLLINS, COL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

A CONTRIBUTION TO THE STUDY OF THE CONSTITUTION OF THE HYDROXYAZO COMPOUNDS. THE ACTION OF UNSYMMETRICAL BENZOYLPARATOLYLHYDRAZINE UPON BENZOQUINONE AND ITS HOMOLOGS.

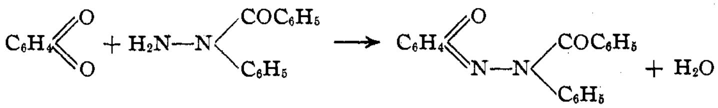
BY WILLIAM McPHERSON AND GEORGE WEATHERWORTH STRATTON.

Received March 6, 1915.

Theoretical.

It has been shown by Nef and McPherson[1] that unsymmetrical (or α) benzoylphenylhydrazine condenses with paraquinones forming the corresponding quinonehydrazones. For example, with benzoquinone the reaction is represented by the following equation:

(1)



$$C_6H_4{<}\begin{matrix}O\\O\end{matrix} + H_2N{-}N{<}\begin{matrix}COC_6H_5\\C_6H_5\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}O\\N{-}N{<}\begin{matrix}COC_6H_5\\C_6H_5\end{matrix}\end{matrix} + H_2O$$

The resulting hydrazones proved to be, not identical, but isomeric with the benzoyl derivatives of the corresponding hydroxyazo-compounds. Thus the hydrazone obtained by the action of unsymmetrical benzoylphenylhydrazine on benzoquinone according to Equation 1 given above, is isomeric with the benzoyl derivative of hydroxyazobenzene prepared by the reaction expressed in the following equations:

---

[1] *Ber.*, **28**, 2418 (1895); *Am. Chem. J.*, **22**, 364 (1899); **25**, 485 (1901).