THE FAVORABLE CONDITIONS FOR THE PRODUCTION OF PROPYLENE.

BY L. J. BONHAM.

The experiments carried out in this department by Dr. W. E. Brown[1] have shown that ethylene is an anesthetic and also that the higher homolog of this series, propylene,[2] appears to be still better in its anesthetic action in that there is a greater range over which complete anesthesia can be satisfactorily maintained. The propylene for these experiments was prepared by the author, and conditions under which the manufacture of this gas could best be made were ascertained. A gas of a high grade of purity was prepared by the reaction of propyl alcohol and phosphoric acid, but this method proved not to be as advantageous as that of the dehydration of propyl alcohol by alumina. In the experiments reported in this paper the most favorable temperature and the conditions of the catalyst which proved most useful were tested.

At first aluminum oxide was purchased and dried in the combustion furnace in which it was afterwards to be employed. This catalyst did not produce as satisfactory a yield as a catalyst prepared as follows; by dissolving pure crystalline aluminum sulphate in water and precipitating $Al(OH)_3$ by the addition of NH_4OH. The precipitate of $Al(OH)_3$ was allowed to settle and the clear supernatant liquid was siphoned off without disturbing the precipitate. Fresh water was added and the precipitate thoroughly agitated. The precipitation and washing was done in large, tall, glass cylinders. The precipitate was washed till the wash water was free from sulphates. The precipitate was then placed in large flat pans in an electric oven at 80–90° C. and the water evaporated. The resulting mass was then removed and broken into pellets of from $1/8$-inch to $1/4$-inch in diameter. These were placed in the electric furnace in a hard, glass tube and heated at 510° C., while a slow stream of dried air was passed over it. The heating was continued until no moisture collected on the cooler part of the glass tube outside the oven, a matter of four or five days in this case as the stream of air was kept very slow. The catalyst was now ready for use.

The propyl alcohol employed was normal propyl alcohol with a boiling point between 96–98° C. The alcohol was displaced from a glass cylinder enclosed in a water jacket by mercury which entered the cylinder through a capillary tube adjusted so that 25 cc. would be displaced in 90 minutes. The displaced alcohol was forced through a second piece of capillary tubing into a vaporizer. This consisted of a small metal tube $1/8$-inch in bore surrounded for a length of 12 inches with a larger brass tube filled with glycerin and containing vents into which thermometers could be placed. The glycerin was heated to 125–130° C., so that the alcohol reaching the tube was immediately vaporized. The vapors were led directly into a hard, glass tube partially filled with alumina, the whole being heated in an electric combustion furnace to the required temperature which was measured by a thermometer whose bulb lay just above the catalyst in the center of the furnace. Temperature was controlled by a rheostat and lamp bank in the circuit. From the

[1] W. E. Brown and V. E. Henderson, *Arch. Inter. de Pharm. et de Ther.*, 28, 258 (1923); W. E. Brown, *Am. J. of Surgery*, Jan., 1924; *Can. Med. Assoc. J.*, March, 1923.

[2] W. E. Brown, *J. Pharm. and Exp. Ther.*, 23, 485 (1924).

furnace the resulting gases and vapors were led through a double condenser which was immersed in an ice and salt mixture. This served to condense any alcohol which passed through the furnace, the water produced in the reaction and any ethers or aldehydes. Then the gas was led to a graduated aspirator type of collecting bottle of 10-liters capacity filled with saturated brine solution; previously saturated with propylene. As the gas was formed, the salt solution was allowed to flow out of the collecting bottle. A manometer was connected to this circuit so that the pressure was kept practically at zero. The brine was re-collected and used over again. Previous to any of the runs reported below the precaution was taken to see that the whole system was filled with propylene gas.

It has been shown by R. Pease and C. C. Yung,[1] that in the catalytic dehydration of ethyl alcohol by alumina, the temperature is an important factor in determining the amounts and nature of the products from such a reaction. Therefore, it was decided to first conduct a number of runs in which the temperature would be varied. This would serve to indicate the most favorable temperature. The first run of 25 cc. of alcohol was made at 350° C. At each successive run, using the same amount of alcohol a temperature 10° higher than the previous one was used until the temperature reached 460° C. The next and last of the series was made at 510° C. During the run two tests were made at original low temperature, namely 350° C. This was to ascertain whether the increasing impurity was due to a change in catalyst or to the temperature. The results are shown in Table I.

TABLE I.

No.	Temperature.	Vol. of alcohol.	Vol. of gas.	Res. gas impurity.	Vol. distillate.
1	350° C.	25 cc.	7000 cc.	1.5%	7.5 cc.
2	360° C.	25 cc.	7600 cc.	1.5%	8.0 cc.
3	370° C.	25 cc.	7200 cc.	2.2%	8.0 cc.
4	380° C.	25 cc.	6000 cc.	3.5%	8.5 cc.
5	390° C.	25 cc.	7000 cc.	2.2%	8.5 cc.
6	400° C.	25 cc.	7500 cc.	2.5%	8.0 cc.
7	410° C.	25 cc.	7800 cc.	2.6%	7.0 cc.
8	420° C.	25 cc.	7600 cc.	2.9%	7.5 cc.
9	430° C.	25 cc.	7900 cc.	3.3%	7.5 cc.
10	440° C.	25 cc.	8100 cc.	4.1%	7.5 cc.
11	350° C.	25 cc.	3000 cc.	2.9%	4.5 + 15.0 cc.
12	450° C.	25 cc.	8100 cc.	4.5%	7.0 cc.
13	460° C.	25 cc.	8000 cc.	5.3%	7.5 cc.
14	510° C.	25 cc.	8200 cc.	5.9%	7.3 cc.
15	350° C.	25 cc.	3100 cc.	3.2%	3.5 + 15.5 cc.

From the table it can be seen that the yields increase very gradually with an increase in temperature, but show a more marked increase in the amount of impurity. The run at the highest temperature shows four times the amount of impurity of that at the beginning. An interesting feature was the result of the runs repeated at the lower temperature during the series, No. 11 and No. 15. Here the yields fall to less than half, and the amount of impurity decreases almost half. In all the other runs the distillate consisted of a one layer of clear, colorless solution. In these two runs the distillate consisted of two distinct layers, the lower clear and

[1] R. Pease and C. C. Yung, *J. Am. Chem. Soc.*, 46, 390 (1924).

colorless except for a slight cloudiness, the upper of a pale yellow color and possessing a somewhat pleasant and yet penetrating and disagreeable odor. A small portion of this latter fraction boils at room temperature and seems mainly responsible for the odor. Complete analysis of this distillate has not yet been made. Undoubtedly it contains some undecomposed alcohol and other products such as aldehydes and ethers. The distillates were subjected to a very simple, straight distillation and the boiling point extended from 72–98° C. in case of the light yellow fraction, and from 85–95° C. in case of the heavier fraction. The former left a dark brown oily residue in the retort. Each fraction was tested for aldehydes qualitatively by using an ammoniacal solution of $AgNO_3$ made by adding NH_4OH to $AgNO_3$ solution until the precipitate just redissolved. Both fractions gave a positive test but more marked in the lower aqueous layer.

The gas collected was analyzed by absorbing samples in a Hempel pipette over fuming sulphuric in which propylene is completely absorbed.[1] The residual gas representing the amount of impurity, was collected and attempts made to analyze it. It consists of a mixture of saturated hydrocarbons and hydrogen, though the assumption that only propane and hydrogen are present does not account for all the impurity in any case. Such gas mixtures consisting of saturated hydrocarbons and hydrogen are extremely difficult to analyze correctly and no further attempts were made to do so. In any case these inert gases, present in this small quantity in propylene have no noticeably physiological effect.

At the end of this series of runs the catalyst was removed from the oven and replaced with new. The old was entirely black, due to a deposition of carbon. It was assumed from work[2] performed in another department in the University of Toronto on the catalysis of ethyl alcohol using alumina, that the carbon deposited on the catalyst, itself exerts a further catalytic action on the alcohol vapors and on the gas formed and this superimposed action increases the amount of saturated hydrocarbons and H_2 and thus accounts for at least part of the increase in impurities. With continued use of the same catalyst it is impossible to prevent the accumulation and effect of the carbon so deposited. It would therefore seem to indicate that with the continued use of any one lot of catalyst the amount of impurity present in the propylene made would increase.

With a view to establishing the behavior of the catalyst over a period of time at one temperature another series was run in which the temperature remained uniform throughout. A relatively low temperature was chosen, for from the first series it will be seen that the yield of propylene is fairly good and the amount of impurity relatively low. A temperature of from 360–370° C. maintained at 365° C. as nearly as possible, was arbitrarily chosen. Fresh catalyst was used. Sixteen experiments in all were carried out and are contained in Table II.

This second series shows that after the first run the yields are fairly constant, falling off only gradually after several days use. The amount of impurity remains practically constant at 2.5%. Thus the catalyst would retain its activity a fairly long time in commercial manufacturing with a uniformity of yield, and since it is not an expensive material should be very satisfactory in the manufacture of propylene from propyl alcohol.

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[1] Berthelot, *Annales de chemie et de Physique*, [7] 4, 104.

[2] Boswell and Dilworth, now going to the press.

TABLE II.   TEMPERATURE 360–370° C.

No.	Vol. of alcohol.	Vol. of gas.	Residue.	Vol. distillate. I.	II.
1	25 cc.	8000 cc.	2.4%	6.0 cc.	0.0 cc.
2	25 cc.	5100 cc.	2.3%	8.0 cc.	8.5 cc.
3	25 cc.	5050 cc.	3.3%	6.0 cc.	6.5 cc.
4	25 cc.	5200 cc.	3.3%	5.5 cc.	6.5 cc.
5	25 cc.	4900 cc.	3.4%	4.75 cc.	7.25 cc.
6	25 cc.	5100 cc.	3.5%	5.0 cc.	7.74 cc.
7	25 cc.	5050 cc.	2.3%	5.5 cc.	8.0 cc.
8	25 cc.	5000 cc.	3.8%	5.0 cc.	8.0 cc.
9	25 cc.	4750 cc.	2.4%	5.5 cc.	10.5 cc.
10	25 cc.	5200 cc.	2.3%	6.0 cc.	9.0 cc.
11	25 cc.	4950 cc.	2.5%	5.25 cc.	8.75 cc.
12	25 cc.	4750 cc.	3.8%	4.75 cc.	9.0 cc.
13	25 cc.	4600 cc.	2.3%	5.0 cc.	9.75 cc.
14	25 cc.	4700 cc.	4.5%	4.25 cc.	9.75 cc.
15	25 cc.	4800 cc.	2.4%	5.5 cc.	11.5 cc.
16	25 cc.	4550 cc.	2.4%	5.0 cc.	10.0 cc.
17*	25 cc.	2900 cc.	2.6%	5.0 cc.	13.75 cc.

* Experiment 17—used distillate No. II in place of propyl alcohol.

Just before removal of the catalyst, a trial was made to see if any propylene could be made by passing the lighter fraction of the distillate over it. The result is given in Table II and gives a gas of much the same nature as the alcohol. A smaller volume of gas was produced and a relatively large amount of the fraction passed over unchanged, or at least not converted to propylene, and collects as distillate.

At the end of this series of runs, the catalyst was removed and presented the same black color due to deposition of carbon as in the first series. The carbon is not deposited on the surface only but is found in as great an amount in the middle of the pellets.

A third series of runs was now begun. It was thought that the carbon might be burned off the alumina and allow of its further use, thus cheapening the manufacturing cost of the propylene. Accordingly the alumina was heated about 30 minutes in the strong flame of a blow torch until it glowed white hot. In appearance the catalyst presented the same color as before use, being entirely white. The results are given below.

TABLE III.—USING REGENERATED Al_2O_3.   TEMPERATURE 360–370° C.

No.	Vol. of alcohol.	Vol. of gas.	Residue.	Vol. distillate. I.	II.	Temp.
1	25 cc.	7500 cc.	2.15%	8.25 cc.	0.0 cc.	..
2	25 cc.	7100 cc.	1.8 %	8.0 cc.	1.0 cc.	..
3	25 cc.	7200 cc.	1.6 %	8.0 cc.	0.75 cc.	..
4	25 cc.	7300 cc.	1.6 %	8.5 cc.	0.25 cc.	..
5	25 cc.	7400 cc.	1.5 %	8.5 cc.	0.00 cc.	..
6	25 cc.	7550 cc.	1.65%	8.0 cc.	0.00 cc.	..
7	25 cc.	8200 cc.	2.0 %	6.5 cc.	0.00 cc.	450° C.
8	25 cc.	8250 cc.	2.1 %	7.0 cc.	0.00 cc.	450° C.

Here we see a marked increase in activity of the regenerated catalyst and the production of a purer grade of propylene. The large yields of gas are accompanied by a smaller amount of distillate and there is no second fraction on continued use at

one temperature as was obtained before. An increase in the temperature results in a slight increase in volume of gas as well as a slight increase in amount of impurity.

We also used commercial aluminium oxide but in no case got gas of a higher purity than 85% propylene.

SUMMARY.

1. The most favorable temperature for the production of propylene from propyl alcohol with alumina catalysts lies at about 360–370° C.

2. The catalyst can be regenerated by burning off the carbon deposit.

3. Propylene of a high grade of purity can be readily prepared by this method.

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THE SYNERGISTIC ACTION OF CAMPHOR IN PHENOL POISONING.

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Poisoning by Phenol is still sufficiently frequent to render a knowledge of appropriate measures of treatment important. Here, as with practically every other orally administered poison, evacuation of the stomach is probably the most valuable therapeutic measure. Emetics may be unsatisfactory for this purpose; either because of the anesthetic action of the poison on the mucous membrane of the alimentary tract rendering reflex emetics ineffective; or because of the depression of the central nervous system which occurs after sufficient absorption of the phenol has taken place. The services of a physician are often obtained only after the lapse of much valuable time and the average pharmacist is unfamiliar with the simple technic of gastric lavage. Therefore, the announcement by E. D. Wilson[1] that in Spirit of Camphor we have a valuable antidote for phenol is deserving of especial attention.

Apparently, Wilson's recommendation is unsupported by experimental evidence. He reasons that, since phenol-camphor mixtures are relatively free from irritant properties, the camphor must combine with and neutralize the phenol. Similar theorizing was responsible for the former belief that alcohol is an antidote for phenol, but it has been conclusively shown that alcohol is in no sense an antidote for the systemic toxic action of phenol. A clear distinction should be made between the purely local action of phenol, elicited when the drug comes into contact with the tissues, and the systemic action, manifest only after absorption from the alimentary tract or other sites. It is true that alcohol renders phenol much less irritant locally and may be used successfully in the treatment of local burns by the poison, but this is simply due to the great solvent power of alcohol for phenol. Systemically, alcohol and phenol resemble each other in their power to depress the central nervous system, and it is a simple matter to show that alcoholic solutions

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[1] *Practical Druggist*, May, 1924, p. 18.