

(artificial light is relatively safe, but daylight must be excluded) precipitated with six volumes of acetone. The covered vessel was kept in the dark for one or two hours, then the contents filtered. The residue on the filter was washed with acetone and air dried away from light. So prepared, piperidine metavanadate is very pure and does not need further purification. The yield is 2.0 g. or about 98% of the theoretical. Purification can be effected by dissolving in water and precipitating with acetone.

Pure piperidine metavanadate is obtained as a white powder made up of small colorless plates. It is readily soluble in from five to six parts by weight of water at room temperature. It is rather soluble in alcohol, but quite insoluble in acetone, ether, benzene, chloroform and carbon tetrachloride. Piperidine metavanadate as prepared contains no water of crystallization and, protected from light, does not lose piperidine in a vacuum desiccator over sulfuric acid.

Anal. Calcd. for $C_5H_{11}N \cdot HVO_3$; V, 27.54; N, 7.57. Found: V, 27.65, 27.49, 27.51; N, 7.54, 7.40.

Exposure of Samples to Light.—Piperidine metavanadate behaves similarly whether exposed to light uncovered or under glass, Pyrex or quartz. Its water solutions in sunlight become black colloidal solutions. The metavanadate in suspension in piperidine or benzene becomes black in light. Chloroform and carbon tetrachloride in light cause side reactions. Ammonium metavanadate is unaffected by light.

Spectrographic Study of Piperidine Metavanadate.—Piperidine metavanadate was spread evenly on a glass

slide and exposed two hours to the ultraviolet radiation of a quartz mercury arc dispersed by a quartz monochromator. The first darkening was visible in two or three seconds at λ 365 m μ .

The spectral absorption measurements were made by the equal density photographic method using micro-Baly tubes, a Judd-Lewis quartz photometer, a Hilger quartz spectrograph, and a tungsten-steel spark. Water solutions of piperidine metavanadate were used.

We are greatly indebted to Rollin D. Hotchkiss for his assistance.

Summary

1. The new compound piperidine metavanadate has been prepared and found sensitive to ultraviolet light but not to the visible spectrum. On exposure to ultraviolet light the white compound becomes brown or black.

2. The light-reaction is a reduction process, reversible by oxidizing agents.

3. The ultraviolet absorption spectrum of piperidine metavanadate has been obtained. The absorption of ultraviolet light by piperidine metavanadate is very much greater than that by piperidine.

NEW HAVEN, CONN.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

Kinetics of Ethylene Polymerization¹

BY H. H. STORCH²

At pressures not very much greater than one atmosphere, the polymerization of ethylene results in the production of considerable quantities of propylene. In fact, Lenher³ seems to believe that propylene is a primary product of the reaction. Lenher also reports that small amounts of oxygen accelerate the reaction. A study of Pease's data⁴ shows that there is a definite increase in the fraction of ethylene reacting per unit time at constant pressure with increasing total time of reaction. This apparent autocatalysis is much greater in the earlier stages of reaction (as shown by the data given below) than in the experiments of Pease.

In the experiments to be described in this

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(3) Lenher, *THIS JOURNAL*, **53**, 3752 (1931).

(4) Pease, *ibid.*, **53**, 613 (1931).

paper, an attempt was made to remove oxygen completely and to study the change in composition of the products with time of contact, using a static system and sufficiently short contact times so that only 0.2–2.0% of the ethylene reacted.

Preliminary experiments amply confirmed Lenher's observation concerning the accelerating effect of oxygen. Using ethylene of the grade prepared for anesthesia, it was found that repeated fractional distillations were insufficient to remove oxygen completely, as judged by subsequent condensation of the ethylene on a large surface of metallic sodium and comparison of its polymerization rate with that of ethylene not treated with sodium. In all later experiments the ethylene, after careful fractionation, was stored in a five-liter flask to the outlet of which was attached a 2.5 × 23 cm. tube filled with glass wool covered with "sputtered" sodium. The

latter was prepared by alternating small lumps of sodium with layers of glass wool, evacuating at about 300° until the glass wool was completely covered with a bright layer of sodium and the pressure reduced to about 10^{-4} mm.

Experiments in which oxygen was added to the purified ethylene indicated that 1 molecule of oxygen caused about 85 additional molecules of ethylene to polymerize (at 377° and 141.5 cm. C_2H_4 pressure, 0.02% oxygen resulted in about twice the yield obtained in the absence of oxygen with two hours contact time). Since it has not been possible thus far to be sure that a completely oxygen-free gas has been obtained, the possibility remains that the autocatalysis is in some fashion connected with the accelerating influence of oxygen.

The reaction vessel was a Pyrex tube 5.75 cm. i. d. \times 67 cm. long, whose volume at 27° was 1700 cc. Of this volume not more than about 5 cc. was outside the mercury vapor bath which was used to obtain a constant temperature. A thermocouple well of about 5-mm. Pyrex tubing was placed in the center of the vessel so that temperatures could be measured throughout the entire length of the reaction zone. Except for a gradient of about 1° in the bottom 2-3 cm. of the reaction tube the temperature was constant to within 0.2° . The 1° gradient was due to the fact that insufficient wall space was allowed for dissipation of superheat.

The experimental procedure was as follows. A sufficient quantity of ethylene was condensed in a small bulb surrounded by liquid air and subsequently allowed to vaporize until the previously evacuated reaction vessel was filled to 141.5 cm. pressure. This pressure was chosen because a convenient rate of reaction could be obtained in the temperature range 350 – 400° , all of the experiments being conducted at this pressure. Filling required about two minutes, and the reaction times were measured from the time when the vessel was half filled. Pressure measurements were made with an open arm manometer, but precise measurement was not attempted, since it was planned to use the volume and analysis of the products as the data for kinetic interpretations. When the selected time interval had been completed, the contents of the reaction vessel were rapidly (within about half a minute) condensed by opening a vacuum stopcock leading to a glass bulb immersed in liquid air. Under the experimental conditions chosen no hydrogen or saturated hydrocarbons were produced, the product consisting entirely of mono-olefins. The bulb in which the ethylene and reaction products were condensed contained a center thermocouple well, with a gas inlet tube surrounding the latter and a plug of glass wool packed between the inlet tube and the outer wall of the bulb to prevent loss by spattering during distillation. An aluminum block containing a hole into which the distillation tube fitted served as a thermostat. The latter was cooled to liquid-air temperatures and subsequently permitted to warm up to -150° , at which temperature the unreacted ethylene was distilled into an adjoining bulb kept at liquid-air temperature. Repeated

trials showed that the ethylene could be removed practically completely in one distillation with a loss of only about 1% of the propylene. After this initial distillation the volume of the products was measured (by noting the pressure in a 125-cc. calibrated receiver) and then rapidly transferred (by condensation with liquid air) into a 1-liter storage vessel sealed off with a mercury valve. In this fashion the time of contact of the olefins with stopcock grease was reduced to a minimum.

The experiment was then repeated until sufficient (150–200 cc. of gas) product had been collected for fractional distillation. Before fractional distillation ethylene was again separated as described above. In no case was more than about 2% of ethylene found in the sample. A vacuum-jacketed unpacked⁵ column about 3 mm. i. d. and 35 cm. long was used for reflux distillation. The boiler had a volume of about 2 cc., and all connections (to manometers and receiving vessels) were constructed to keep the "dead space" down to a minimum value. Mercury valves were necessary to seal off the receiving vessels and avoid loss of the olefins upon storage. A three-junction copper-constantan couple was used to measure the reflux temperature. A thin brass sheath surrounding the outside of the column provided the necessary temperature gradient in the column.

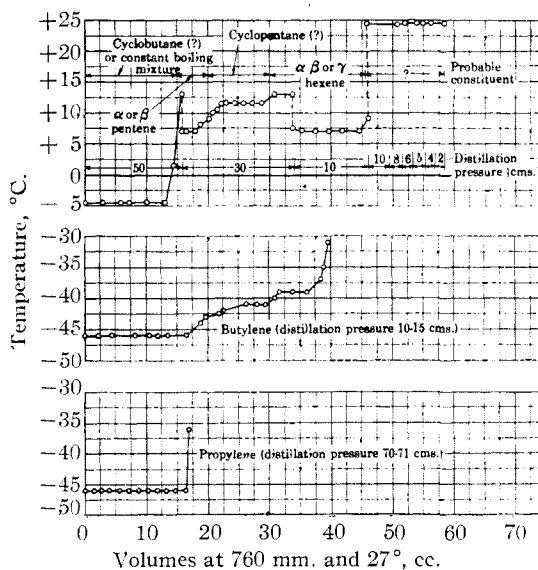


Fig. 1.—Distillation curves for one-hour product; volume of sample, 123 cc.

The data obtained concerning the amounts and nature of the product for one, two and three hours at 377° and 141.5 cm. pressure are given in Table I. The distillation data from which the analyses of the product were deduced are given in Figs. 1, 2, and 3. Figure 4 presents a vapor pressure chart for various hydrocarbons, and the location of the blackened circles on this chart

(5) The thermocouple well was extended into a fine (about 0.5 mm.) glass rod extending through about 20 cm. of the column.

TABLE I
POLYMERIZATION PRODUCTS OF ETHYLENE AT 377° AND
141.5 CM.

| Time of contact, hours | 1 | 2 | 3 |
|---|------|------|------|
| Yield, cc. (at 27° and 76 cm.), per expt. | 3.7 | 16.4 | 37.1 |
| Pressure drop, cm. | 0.35 | 1.5 | 3.35 |
| Propylene, vol. % | 13.8 | 28.4 | 30.5 |
| Butylene, vol. % | 31.7 | 32.0 | 24.2 |
| "Cyclobutane," vol. % | 12.6 | 2.1 | 5.9 |
| Pentenes, vol. % | 4.1 | 6.1 | 6.6 |
| "Cyclopentane," vol. % | 8.1 | 11.5 | 4.0 |
| Hexenes, vol. % | 12.6 | 8.9 | 14.4 |
| Higher olefins, vol. % | 10.1 | ... | 2.3 |
| Unaccounted for, vol. % ^a | 7.0 | 11.0 | 12.1 |
| Av. contraction factor ^b | 2.28 | 1.83 | 2.03 |
| Yield, cc. (at 27° and 76 cm.) calcd. from contraction factor and press. drop | 2.8 | 18.6 | 33.5 |

^a Probably loss by absorption in stopcock grease.

^b Calculated upon the assumption that the percentage "unaccounted for" is propylene, and that the higher olefins have an average of 8 carbon atoms per molecule.

indicates the apparent vapor pressure of the various fractions obtained during the distillations.

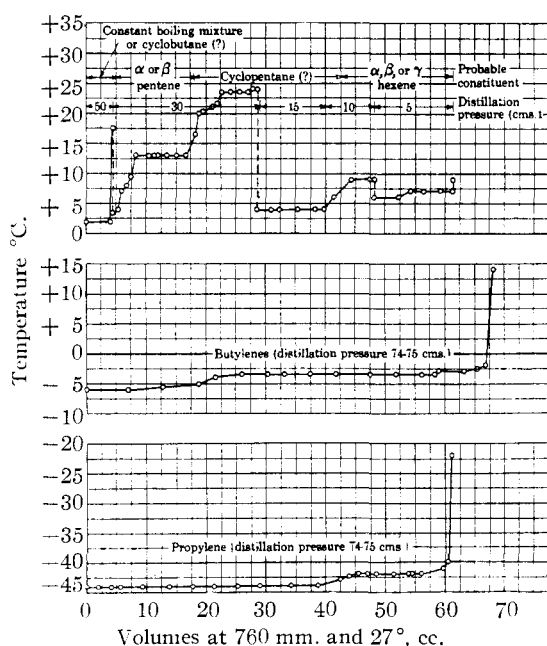


Fig. 2.—Distillation curves for two-hour product; volume of sample, 213 cc.

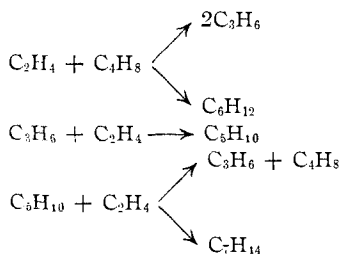
The ratio of propylene to C₄ hydrocarbons (butylenes plus cyclobutane) is 0.31, 0.83, and 1.01, for the one-, two-, and three-hour products, respectively. It is very probable, therefore, that propylene is not a primary product. The

distillation data (especially those for the one-hour product) indicate the presence of both α - and β -butenes. The presence of cyclobutane is questionable, particularly in view of the erratic variation in the amounts of this constituent at one-, two-, and three-hour contact times. A similar remark may be made concerning cyclopentane. Molecular weight determinations were made on "cyclobutane" + total C₅ + C₆ combined fractions for the one- and two-hour products, by condensing in a small tube, which was then sealed off and weighed; the tube was then cut open, the liquid completely removed, and the tube again weighed. The experimental results are 65 and 73.5 for the one- and two-hour products, respectively, 70 and 69 being the "theoretical" molecular weights based on the analysis as reported. It is apparent, therefore, that if the C₅-C₆ separation is reasonably accurate the "cyclobutane" fraction must be largely C₄. It may, however, be a constant-boiling mixture of C₄ + C₅. Further experiments on the chemical properties of the "cyclobutane" and "cyclopentane" fractions are essential.

The loss of 7-12% of the distillation sample was probably due to absorption by stopcock grease of the cock used to regulate the rate of distillation and that which connected the still to the storage vessels. These cocks were lubricated with ordinary stopcock grease. In future work it is planned to develop a mercury valve that will permit regulation of the distillation rate without greatly increasing the "dead space."

The calculated yield, assuming that the distillation loss was entirely propylene, is lower than the actual yield in the one- and three-hour products. The only possible way to account for this is that the average molecular weight of all of the fractions from "cyclobutane" to "higher olefins" is lower than that indicated by Table I.

Comparison of the yields per hour for the three contact times of Table I shows a marked increase in over-all rate with increasing contact time. Thus the yields per hour are 3.7, 8.2, and 12.4 at the end of one, two, and three hours, respectively. The increase between two and three hours is of the same order of magnitude as that observed by Pease.⁴ Since more than 1% conversion of ethylene was obtained in most of his experiments, no figures are available for comparison with the large increase between the first and second hour. Unquestionably secondary reactions of the following types occur



It is, however, unlikely that such secondary reactions, even if they are much more rapid than

found to be fifty-four minutes for 393° and seven one-half hours for 351°. When compared with two hours for 377°, using the equation $d \ln k/dT = E/RT^2$, the three values obtained for the heat of activation are 41,950, 41,200 and 43,000 calories. These values are considerably higher than Pease's⁴ experimental value of 35,000 calories. It is possible that if the accelerating influence of oxygen were completely eliminated values higher than those obtained above would be found.

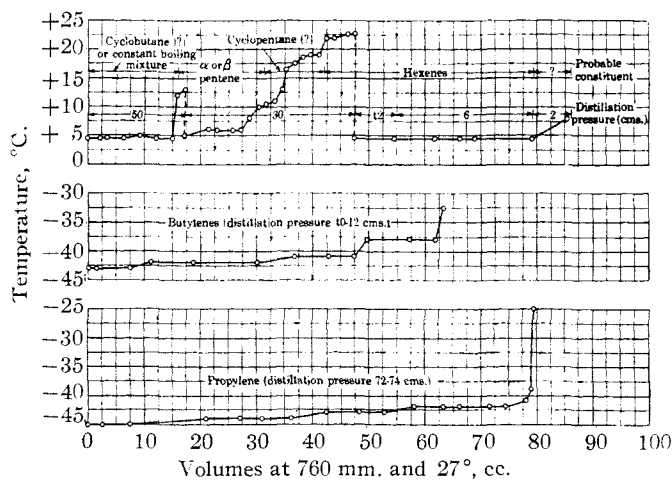


Fig. 3.—Distillation curves for three-hour product; volume of sample, 260 cc.

Table II contains the results of some preliminary experiments, in which the distillations were not completed beyond the butylene fraction.

Comparison of the two-hour tests of Table I with the asterisked test of Table II shows that prolonged contact of gaseous ethylene with metallic sodium was not as efficient as condensation of the ethylene on a sodium surface. The tests of Table I are nevertheless self-consistent, for the same mode of ethylene preparation was used in all.

the primary butylene formation, can account for the very large increase in rate during the second hour. Indeed, it seems impractical at the present time to attempt to account for such an increase. Its explanation must await further data on the character and rates of the secondary reactions.

It is planned to repeat the experiments of Table I, making a more strenuous effort to obtain oxygen-free ethylene, substituting mercury valves for the remaining stopcocks wherever possible, and using starch-glycerin

To obtain data from which the heat of activation of the reaction may be calculated experiments were conducted at 393 and 351° for comparison with the two-hour tests at 377°. The times necessary to obtain the same yield (cc. of product) were determined after several trials for each of the two new temperatures. These were

lubricant where a stopcock is indispensable. It was, however, considered desirable to publish the present data not only because the results thus far

TABLE II

YIELDS AND ANALYSES OF ETHYLENE POLYMER AT 377° AND 141.5 CM. PRESSURE. PRELIMINARY EXPERIMENTS

| Time of contact, hours | 1 | 2 | 2* | 3 |
|---|------|------|------|------|
| Propylene, % by vol. | 31.7 | 31.0 | 15.6 | 33.7 |
| Butylene, % by vol. | 31.9 | 34.2 | 39.4 | 29.3 |
| Yield, cc. (at 27° and 760 mm.) per expt. | 6.0 | 20.5 | 15.8 | 53.5 |

* In these two-hour tests marked with an asterisk the ethylene was condensed on a large surface of metallic sodium, in all of the other tests of Table II, only redistillation of the ethylene was used to remove oxygen.

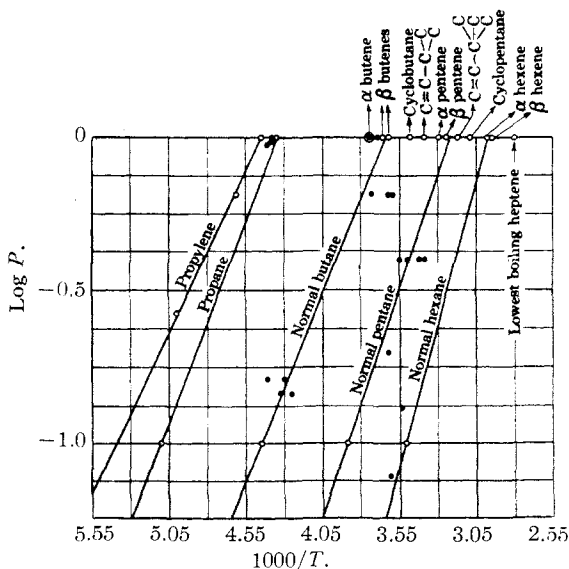


Fig. 4.—Vapor pressures of hydrocarbons: O, values taken from literature; ●, values taken from distillation curves of Figs. 1, 2 and 3.

are of sufficient interest to justify such publication but also because there is little assurance that sufficient funds will be available for further experiments.

The writer wishes to acknowledge the many helpful criticisms made by Dr. L. S. Kassel.

Summary

Data are presented concerning the composition and amounts of products from ethylene polymeri-

zation at 377° and 141.5 cm. pressure. These indicate that the primary product is butylene and that propylene formation is secondary. Minute amounts of oxygen accelerate the reaction. There is also a large increase in over-all reaction rate with time of contact. In the temperature range 350–400° the heat of activation was found to be about 42,000 calories.

PITTSBURGH, PA.

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[CONTRIBUTION FROM LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

Separation of Photochemical and Thermal Action in the Photobromination of Cinnamic Acid¹

BY WALTER H. BAUER AND FARRINGTON DANIELS

The addition of bromine to the double bond of cinnamic acid under the influence of light offers a means for studying chain reactions. It has been investigated before,^{2,3,4} but in the present work accurate determinations of the quantum yield as a function of the concentration of bromine at different temperatures have been made. Some of the earlier work may now be interpreted differently in view of the concentration effects described here. It has been found that dilution decreases the length of the chain, so that under extreme dilutions the primary photochemical reaction stands alone. Under these conditions the yield of one molecule per quantum is obtained in agreement with the Einstein relation, and the reaction is not affected by temperature.

Experimental Procedure

The monochromator was built around a hollow glass prism of 60°, 12 cm. on an edge, filled with ethyl cinnamate. Light was furnished by a capillary, mercury-vapor lamp⁵ of high intensity. The optical train contained two lenses 15 cm. in diameter and 16 cm. in focal length, a series of slits, and a front-silvered mirror in Wadsworth mounting. The prism table was rotated with a machinist's micrometer. At the exit slit, 0.5 mm. wide, the energy intensity was about 20,000 ergs per second for the mercury lines at 436 m μ . Movement of the slit image by 0.5 mm. caused the intensity to drop to 1% of

its former value. Entry and exit slits were cut in thin silver foil and mounted on heavy aluminum plates. Adjustable slits of brass were unsatisfactory because the intense radiation caused them to expand and change the width of the slit.

The exit beam, rendered parallel with a convex lens, passed through the reaction cell in a large thermostat of clean water. The reaction cell was of plane, polished quartz, 1 cm. wide, 1.9 cm. thick and 9 cm. high. A long neck permitted the cell to be immersed deep in the thermostat. The 2-mm. stirrer with small vanes of quartz was rotated rapidly just above the region of illumination. The large thermopile, having a receiver area 9 × 33 mm., was constructed in this Laboratory. It was set in a heavy aluminum case, back of the cell in a box immersed in the thermostat. Calibration in absolute units was effected with radiation lamp No. 132 from the U. S. Bureau of Standards.

Kahlbaum's cinnamic acid was recrystallized from alcohol. It melted at 133°.

The bromine, Mallinckrodt analytical quality, was refluxed with potassium bromide and distilled, twice distilled from barium oxide, and further purified by crystallization. Two different preparations gave identical quantum yields.

Carbon tetrachloride was refluxed in 10-liter lots for six hours with alkaline permanganate, washed, and distilled from calcium chloride, and finally distilled from phosphorus pentoxide or metallic sodium. This material showed some slight absorption of the 313 m μ line of mercury. Bovis⁶ states that such absorption is probably due to a trace of carbon disulfide, but its presence could not be detected by other tests. Different samples of carbon tetrachloride used over a period of two years showed no difference in the behavior of the reaction.

The extent of the reaction was determined by titrating the decrease in bromine. Stock solutions of bromine and of cinnamic acid in carbon tetrachloride were diluted and mixed in equal portions. The control solution was kept in a blackened quartz flask set deep in the thermostat.

(1) Presented at the meeting of the American Chemical Society, Chicago, Illinois, September 14, 1933; also *THIS JOURNAL*, **54**, 2564 (1932). More complete details may be found in the Ph.D. thesis of Walter H. Bauer, filed in the Library of the University of Wisconsin in June, 1933.

(2) Purkayastha and Ghosh, *Quart. J. Indian Chem. Soc.*, **2**, 261 (1926); **4**, 409 (1927); **4**, 553 (1927).

(3) Purkayastha, *ibid.*, **5**, 721 (1928).

(4) Berthoud and Beranek, *J. chim. phys.*, **24**, 213 (1927); *Helv. Chim. Acta*, **10**, 289 (1927); **13**, 385 (1930).

(5) Daniels and Heidt, *THIS JOURNAL*, **54**, 2381, 2384 (1932).

(6) Bovis, *J. phys. radium*, **10**, 267 (1929).