phosphorous and phosphoric acids in acid or alkaline solution was found to occur beyond the limits of experimental error. The results indicate that if the phosphorus atoms in hypophosphoric acid are equivalent, the equilibrium constant for the formation of hypophosphoric acid from phosphorous and phosphoric acids is less than 8×10^{-5} mole^{-1} liters at 25° in 5.6 formal hydrochloric acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Instability of Liquid Isobutene

BY EDWIN E. ROPER

In the course of measurements of the vapor pressure of a number of unsaturated hydrocarbons, the results of which are to be presented in a later paper, it was found that the vapor pressure of originally pure isobutene (2-methylpropene) decreases over a period of time and from this aged material a relatively high-boiling liquid was isolated. The most probable explanation of this instability of isobutene is that a polymer is formed. Since there appears to be no mention in the literature of any such uncatalyzed polymerization of isobutene, although it is well known that in the presence of certain catalysts isobutene is converted into polymers,[1] and since we do not plan to continue the study of this behavior further, it appears worth while to present our findings at this time.

Experimental

Apparatus.—A simple static system was used, consisting of a small (*ca.* 5 cc.) vapor pressure tube immersed in an ice-bath, which was maintained at 0.000 ± 0.001° for the observations. The washing procedure required to establish this temperature reproducibility in the ice-bath has been described.[2] The pressure was measured on an absolute manometer, of 15-mm. inside diameter Pyrex tubing, by a high grade cathetometer; meniscus corrections were determined for each observation and the pressure converted to international millimeters[3] (int. mm.) of mercury. Accessory apparatus included vacuum line, fore and condensation pumps, McLeod gage and a system of stopcocks; the manometer had a reservoir sealed on at the bottom, allowing the U to be used as a mercury cut-off, which was the only access to the vapor pressure system, so that no stopcocks were exposed to the vapor for long periods of time.

Material.—Four samples of isobutene were available. Sample D was from Dr. Harold S. Davis; it had been prepared by the dehydration of *t*-butyl alcohol by means of oxalic acid and purified in a Davis[4] low-temperature fractionating column. The boiling point range of this sample was given as ±0.05°. Sample R was one we had prepared by the method described by Davis,[4] with a boiling range of *ca.* 0.5°. Sample K, obtained from Professor Kistiakowsky of these Laboratories, had been highly purified for a determination of the heat of hydrogenation;[5] the consistent value of this heat of reaction for different fractions from the distillation,[5] the method of distillation,[5] the value of the freezing point,[5,6] and our vapor pressure measurements in conjunction with isothermal vaporization, gave indication of exceptional purity of the sample, of the order of 99.9%. Sample F was presented to us by Professor Forbes of these Laboratories; it had been prepared by the same investigators as had sample K and was the remnant of the material used in the photochemical investigation of Forbes and Nelson.[7] The boiling range was the same as that for sample K, namely, 0.02°. Samples K, F and R were dried by a physical method, which consisted of a filtration of the liquid through glass wool held at low temperatures;[8] this effectively dried the hydrocarbon and possibly removed some of the polymer. The samples were stored in the liquid phase in all-Pyrex glass containers, fitted with a glass internal break-off seal, externally operated by an electromagnet. High vacuum technique was used in all operations of filtering and transferring.

Procedure.—Immediately previous to the vapor pressure determinations, a distillation from the storage container at −80°, to a bulb on the vapor pressure line, via the manometer-cutoff, at −188° was carried out; this operation required some time, because of the low vapor pressure of the hydrocarbon at −80° (12 mm.). The first few tenths of a cc. that distilled was discarded, as was the last portion. In the subsequent examination of the latter, the container having been removed from the vacuum line, it was noticed that a small amount of residue, with a distinctive odor, was left after the admixed isobutene had been allowed to vaporize into the atmosphere; this residue was liquid at −80° and crystalline at −188°. It was obvious that the residue had formed during the several months of storage in the glass container, for during the

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[1] (a) Ellis, "The Chemistry of Petroleum Derivatives," The Reinhold Publishing Co., New York, N. Y., Vol. I, 1934, pp. 315, 378, 600; Vol. II, 1937, p. 641; (b) Whitmore and Wrenn, THIS JOURNAL, **53**, 3136 (1931); (c) Tongberg, Pickens, Fenske and Whitmore, *ibid.*, **54**, 3706 (1932).

[2] Roper, THIS JOURNAL, **60**, 866 (1938).

[3] Burgess, *Bur. Standards J. Research*, **1**, 635 (1928).

[4] Davis, *Ind. Eng. Chem.*, *Anal. Ed.*, **1**, 61 (1929).

[5] Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 876 (1935).

[6] Compare with Todd and Parks, *ibid.*, **58**, 134 (1936).

[7] Forbes and Nelson, *ibid.*, **59**, 693 (1937).

[8] Roper, *Ind. Eng. Chem.*, *Anal. Ed.*, **9**, 414 (1937).

initial treatment previous to storing, the same type of distillation had been performed.

The vapor pressure measurement was then carried out with this freshly distilled material and a small but definite decrease with time was observed. Part A of Fig. 1 shows the data for the first trial, using sample K. Some of the observations appear to be erratic; the only explanation that can be advanced is that possibly the pressure readings were taken too soon (*ca.* fifteen to thirty minutes) after the washing operation on the ice-bath. The ice-bath was replenished at suitable intervals so that 0.000 ± 0.004° was always maintained throughout the duration of the trial; previous to making an individual pressure determination, the ice-bath was brought to within ±0.001° of 0.000° by the washing procedure.[2] ±0.001° is equivalent to ±0.03 mm. in the vapor pressure as determined from the slope of the vapor pressure curve at 0°. At the end of the trial, an attempt was made to free thoroughly the system from polymer, by pumping for a long period.

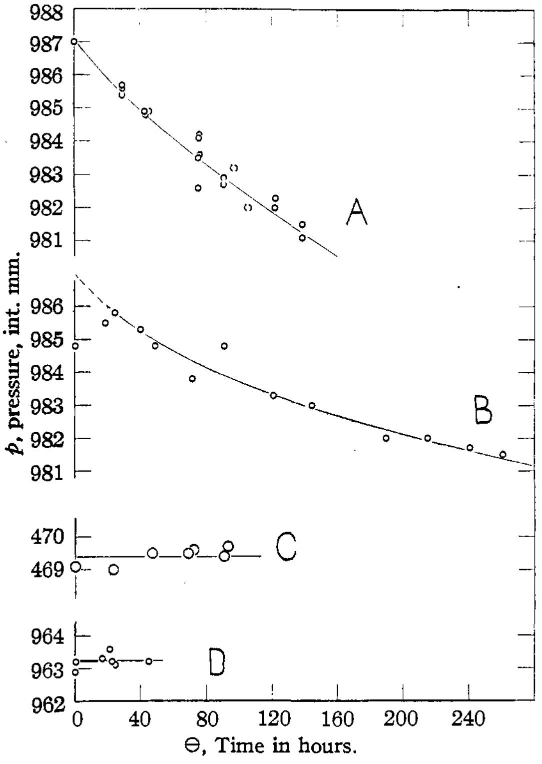

Fig. 1.—Comparison of results. Part A represents the vapor pressure change for isobutene, first trial, part B for the second trial; part C shows the data for the non-saturated vapor of isobutene. Part D gives data obtained for the vapor pressure of 1-butene. The diameters of the circles are 0.2 mm. in parts A, B and D, and 0.3 mm. in part C.

The identical apparatus had been in use for several months previous to this trial and no leaks were apparent. Nevertheless, it appeared necessary to investigate this point and accordingly the pressure was decreased to 470 mm. and readings made on the pressure over a period of time. The varying room temperature gave rise to different pressures of the non-saturated vapor but by means of the average change in p with T, the pressures were corrected to a common temperature. Part C, Fig. 1, presents the results; the data indicate that no leak existed and also that the hydrocarbon is stable in the vapor phase at this temperature.

The vapor pressure trial was then repeated, using a fresh sample of isobutene distilled into the vapor pressure bulb by the −80 to −188° procedure. Part B, Fig. 1, shows the results, which do not exactly parallel those of the first trial but the general behavior is the same. The low values at the commencement are not explainable.

Over a year after the conclusion of the above trials, sample K, which had been stored in glass, was distilled into a new vapor pressure system in the manner outlined. Again a small amount of the high-boiling liquid remained in the container. No attempt was made to study the change in the vapor pressure with time although it was observed, but four determinations were obtained for the freshly distilled material, averaging 988.6 ± 0.3 int. mm. at 0.000 ± 0.001°.

In distillations after the manner described, of samples D, F and R, a residue of the high-boiling liquid from each has been noted, providing the hydrocarbon sample had been stored for some time in the liquid phase. A second distillation, immediately following the first, reveals no trace of the high-boiling liquid, nor does a distillation on material which has been stored in the gas phase. From sample F 0.25 g. (1.5 weight per cent.) and from sample R 0.40 g. (0.8 weight per cent.) of polymer was secured by collecting the residue remaining in the tube after a −80 to −188° distillation.

Investigation of the High-Boiling Liquid.—A rough freezing point was obtained by means of liquid air and a small pentane thermometer. The ranges −105 to −115° and −100 to −120° were found for the material from samples F and R, respectively. The refractive indices were kindly determined by Dr. J. B. Conn of these Laboratories, and $n^{20}\text{D}$ found to be 1.435 and 1.397 for the material from samples F and R, respectively. The product took up bromine (in carbon tetrachloride solution) first by addition and then shortly thereafter by substitution.

Discussion

With such small amounts of the high-boiling liquid available, purification and accurate boiling and freezing points were not feasible, especially if a mixture is present, for separation by distillation probably would prove to be impossible due to the similarity of the boiling points of the components; the freezing point would be inconclusive if separation were not effected. The physical properties of the two components of di-isobutylene as determined by Tongberg, *et al.*,[1c] are as follows: for 2,4,4-trimethylpentene-1 the freezing point is −93.6°, $n^{20}\text{D}$ 1.408, for 2,4,4-trimethylpentene-2 the freezing point is −106.5° (another form at −108.3°), $n^{20}\text{D}$ 1.416. For triisobutylene, $n^{20}D$ 1.431;[1c] since there are at least three hydrocarbons present,[9] a freezing point is meaningless, except for the equilibrium mixture. However, a hydrocarbon of the formula $C_{12}H_{24}$ should freeze in the vicinity of −20° (±20°). A comparison of the freezing points and refractive indices of the high-boiling liquid with those given above for three possible polymerization products shows that no very definite conclusion can be drawn as to the exact nature of the high-boiling liquid. According to the mechanisms given by McCubbin and Adkins[10] for the addition of isobutene to isobutene, four dimeric products are possible, namely, 2,4,4-trimethylpentene-1, 2,4,4-trimethylpentene-2, 2,5-dimethylhexene-1 and 2,5-dimethylhexene-2.

There does not seem to be any possibility that accidental contamination with some catalytic material can be the cause of this polymerization, since it has been observed with samples from three sources, prepared by two different methods, and under varying conditions. In view of this instability, the properties and reactions of isobutene, to a minor degree, will depend upon its past history.

For the other three butenes, no residue has ever been found in the −80 to −188° distillation and the data obtained on the vapor pressures do not show evidence of change with time. These vapor pressure results were not collected for this particular illustration and it would have been desirable to extend the time of observation; unfortunately, this was not possible. Part D, Fig. 1, shows the results obtained with 1-butene, and gives some idea of the reproducibility of the measuring system. For 1-butene, *trans*-2-butene and *cis*-2-butene vapor pressures at 0.000 ± 0.001°, an analysis of the results indicates that the extreme variation is 0.4 mm. or less, the means ±0.1 mm., measured over forty-five, twenty-nine and twenty hours duration, respectively; these three hydrocarbons were prepared by the collaborators of Professor Kistiakowsky.[5]

Thermodynamic data are available for the polymerization of liquid isobutene to the liquid dimer, trimethylpentene. By utilizing the data of Parks and co-workers,[6,11] the free energy of formation of the liquids may be approximated closely. The value of the equilibrium constant calculated from the free energy for the dimerization reaction is about 10^7 times greater than the value calculated from the weight concentration of high-boiling liquid found, making the assumption that it is trimethylpentene. Two factors could cause such a discrepancy: non-attainment of equilibrium, and a different mechanism than simple dimerization to trimethylpentene. It appears very likely that both factors are operative, although from the observed freezing points and the qualitative observations on the volatility of the high-boiling liquid, not a great quantity of trimer can be present. It is worth noting that the free energy changes for the three possible isomerization reactions of isobutene are all positive values, although rather small, so that isomerization to 1-butene or 2-butene should not occur spontaneously to complicate further the course of this polymerization reaction.

I wish to thank Professor Arthur B. Lamb, under whose direction this work was carried out, for facilities placed at my disposal and for advice in preparing this manuscript. I am grateful to him and to Dr. H. S. Davis, Professor G. S. Forbes, Professor G. B. Kistiakowsky and Dr. J. R. Ruhoff for making available the hydrocarbon samples.

Summary

It has been shown that isobutene in the liquid phase forms a high-boiling liquid, upon standing, which probably is a polymer, with certain evidence pointing to dimerization as the first step. At 0° this reaction causes a lowering of the pressure of the saturated vapor of pure isobutene to the extent of about 0.6%. The other three butenes do not exhibit such behavior.

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[9] McCubbin, THIS JOURNAL, 53, 356 (1931).

[10] McCubbin and Adkins, *ibid.*, 52, 2547 (1930).

[11] Parks, Todd and Shomate, *ibid.*, 58, 2505 (1936).