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

Kinetics of Ethylene Polymerization. II[1]

BY H. H. STORCH[2]

Effect of Oxygen

In a preliminary paper[3] the author showed that the rate of ethylene polymerization was increased markedly by minute amounts of oxygen. Subsequent experiments, which are described below, were designed to eliminate this impurity and to redetermine the rate, temperature coefficient, and character of primary products in oxygen-free ethylene.

Several procedures were tried in an effort to obtain oxygen-free ethylene, namely: (1) passage over a large surface of metallic sodium. This is the method used in preliminary experiments.[3] (2) Removal of oxygen from redistilled "anaesthesia" grade ethylene by slow passage over reduced metal oxide and thoria mixtures, such as Ni–ThO_2 (used at 25–150°) and Cu–ThO_2 (used at 300–350°). These mixtures contained about 5% ThO_2 and were prepared by precipitation with ammonia from a solution of the nitrates and subsequent heating of the washed hydrated oxides at 100 to 200° and finally at 500° before use.

(3) Preparation of ethylene by the reaction of ethylene bromide and zinc, both reactants being outgassed carefully by heating and evacuation before the reaction was started. The reaction rate was controlled by the rate of distillation of the ethylene bromide onto the zinc. It was found desirable to add about 0.1% of copper to the 40-mesh zinc by washing with a cupric chloride solution. The ethylene was fractionated by distillation before use.

(4) Preparation of ethylene by the dehydration of ethyl alcohol by passage over a thoria catalyst at 350°, the alcohol and catalyst being outgassed by heating and evacuation. The ethylene was fractionated by distillation before use.

All the experiments of Table I were made using the same apparatus[4] and procedure as described in the preliminary paper.[3] In the experiments with ethylene made by procedure 2 the Ni (or Cu) + ThO_2 tube was sealed directly onto an 8-liter storage vessel, so that the ethylene always was passed through the bed of reduced metal oxide plus thoria at a slow rate upon withdrawal from or admission to the reservoir.

TABLE I

POLYMERIZATION RATES OF ETHYLENE PREPARED BY DIFFERENT METHODS

Temperature, 377° Pressure 142 cm.
Reaction volume 1700 cc.

C_2H_4 prepn. procedure no.	1	2 (Cu)	2 (Ni)	3	4
ΔP in 2 hours, mm.	15.0	10.1	10.8	15.7	2.0
Cc. of product (760 mm. and 27°)	16.4	11.0	11.1	17.3	1.8

Because the polymerization rate of ethylene prepared by procedure 4 was so much lower than that of ethylene obtained by any other method, a large number of experiments were made with this ethylene preparation. The rate increased slowly upon prolonged storage of the ethylene, and it was found that detectable amounts of hydrogen sulfide were present in the gas. This compound was probably formed by the reduction of traces of sulfur compounds present in the thoria catalyst. Upon introducing a tube containing sodium hydroxide sticks in the apparatus for procedure 4 to remove hydrogen sulfide from the gas as it left the catalyst tube, the resulting sulfur-free ethylene yielded a polymerization rate about equal to that prepared by procedure 3. It was therefore suspected that hydrogen sulfide was acting as an antioxidant and destroying the accelerating influence of the minute amounts of oxygen present. The origin of this oxygen is somewhat uncertain, especially in procedures such as nos. 3 and 4 (plus sodium hydroxide sticks) of Table I. The preparation and storage apparatus was tested repeatedly after prolonged evacuation, and it was found to be as vacuum-tight as one can reasonably expect without baking at a red heat which is necessary to secure and retain very high vacua. It is probable that very small amounts of oxygen were being desorbed continuously from the glass walls. It is also conceivable that the many necessary operations of the mercury valves "dragged" thin films of gas into the system. Tank nitrogen containing 0.5% oxygen was used to raise the mercury.

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[3] Storch, THIS JOURNAL, **56**, 374 (1934).

[4] Except that all stopcocks were replaced by mercury valves.

After considerable experimentation it was apparent that even if oxygen-free ethylene could be prepared it could not be kept free of contamination by traces of oxygen in the apparatus used. Hence it was decided to add small amounts of ethyl mercaptan to the ethylene used in each experiment and to assume that the reaction kinetics of this mixture is quantitatively identical with that of oxygen-free ethylene.

The plausibility of this assumption was indicated by the following experiments.

Tank ethylene of anaesthesia grade was passed through alkaline pyrogallol, 60% aqueous sulfuric acid solution, and solid potash fragments, and then condensed at liquid nitrogen temperatures. The ethylene was subsequently distilled at about 2 cm. pressure, the first and last thirds of the distillate being discarded. Experiments at 142 cm. C_2H_4 plus 1.4 mm. C_2H_5SH pressure and 393° were made which yielded rate data reproducible to within about 5% of the mean value. The same batch of ethylene was used in all such experiments, the portion used to fill the reaction vessel (about 75% of the total ethylene in the reservoir) being recovered by fractional distillation which separated the ethylene from the polymerization products and from the ethyl mercaptan. After about fifteen experiments with the same batch of ethylene another rate determination was made omitting the mercaptan. The polymerization rate obtained in this experiment was practically identical with that of the last experiment using 1.4 mm. of mercaptan.

It was also found that additions of more than about 0.1 per cent. of mercaptan to the ethylene did not decrease the rate of polymerization any further, hence this concentration of mercaptan was used in all subsequent experiments.

Induction Period

The apparent autocatalytic nature of ethylene polymerization has been indicated elsewhere.[3] Similar results were obtained with ethylene to which 0.1% of ethyl mercaptan had been added. This is shown in Table II. The yields were measured as described in the first paper.[3] The data given for item (a) are the average results of eight experiments for the one- and two-hour intervals and of six experiments for the three-hour periods. The average and maximum deviations from the mean are 6 and 10%, respectively, for both the one-hour and two-hour intervals and 3 and 8%, respectively, for the three-hour intervals. The data for the other items in Table II represent single experiments.

The pressure decreases for the second hour are, with the exception of item (c), identical for the various gas mixtures used. This indicates that the same steady state has, in cases (a), (b), (d) and (e), been reached before the end of the first hour.

TABLE II

DATA ON AUTOCATALYSIS IN ETHYLENE POLYMERIZATION

Temperature, 393°. Initial pressure, 142 cm. Volume of reaction bulb, 4400 cm.

Time intervals	a C_2H_4 + 0.1% C_2H_5SH	b a + 1.3 mm. C_3H_6	c a + 1.7 mm. C_3H_6	d a + 1.4 mm. C_4H_8[a]	e a + 4.5 mm. C_4H_8[a]
	Pressure drop in mm.				
First hour	1.6	1.2	2.4	2.4	2.6
Second hour	4.4	4.4	3.6	4.4	4.4
Third hour	3.8	...	...	...	...
	Volume of product, cc. at 760 mm. and 27°				
Two hours	12.1	7.5[b]	11.3[b]	9.8[b]	18.8[b]
Three hours	21.7	...	...	...	...
Time interval ratios	Ratios of pressure drop for different time intervals				
Second/First (hour)	2.8	3.7	1.5	1.8	1.7
Third/Second (hour)	0.87	...	...	...	...

[a] 1-Butene was used in these tests. Similar tests with the low-boiling isomer of 2-butene gave identical results.

[b] Includes any unreacted propylene or butylene. Correction for C_2H_5SH is made in all cases (a) to (e).

The introduction of small amounts of propylene or butylene does not eliminate the increased pressure drop in the second hour compared with that of the first hour. The apparent reduction in the ratio of pressure drop for the second to the first hour in (c), (d), and (e) probably is due to a somewhat more rapid rate of reaction of propylene and butylene with ethylene. In fact, this must be true, for otherwise it would not be possible to explain the smaller volume of the products in items (b), (c), and (d). Item (e) apparently has a larger volume of products than item (a), but unquestionably this is due to the fact that the butylene added initially was almost equal to the amount of polymer obtained in item (a).

The data for the second and third hours of item (a) in Table II, when compared with the similar data in Table I of the preliminary paper,[3] show that the addition of mercaptan apparently has eliminated the autocatalysis after the first hour. The results with varying amounts of mercaptan from 0.05 to 0.15% show that after 0.1% has been added, further additions do not change the pressure decreases in any of the time intervals. Hence it seems that the polymerization reaction may have an induction period of its own, independent of any of the catalytic effects of small amounts of oxygen. The intermediary compounds whose rates of formation result in the induction period are stable enough to survive the condensation of the reaction mixture[5] after about ninety minutes reaction time and subsequent revaporization into the reaction chamber. In such an experiment, using C_2H_4 + 0.1% C_2H_5SH, the reaction rate a few minutes after revaporization was identical with that during the sixty- to ninety-minute interval. This evidence shows that the building up of any chain involving only free radicals or only energy-rich molecules as chain carriers is not responsible for the induction period. It is therefore certain that the rate of formation of a moderately stable intermediate compound must be the source of the induction period. Energy chains or free radical chains may of course be involved also in the reaction mechanism, but they cannot be of any importance in explaining the origin of the induction period.

Temperature Coefficient

The time necessary to obtain the same volume of reaction product at 377° as is obtained in 2 hours at 393° was found to be 4.5 hours. The pressure was the same (142 cm.) in both cases. The activation energy calculated in the usual way from these two data is 43,500 cal. The value previously reported by the author[3] for ethylene prepared by procedure 1 was 42,000 cal., and that reported by Pease[6] for tank ethylene of "anaesthesia" grade was 35,000 cal. It seems reasonable to conclude that the presence of oxygen lowers the apparent heat of activation and that 43,500 cal. is closer to the true value than any of the other values.

A calculation, using $43{,}500 + RT/2$ as the activation energy (rate in pressure units = Const. $T^{-1/2}e^{-E/RT}$) and the average pressure drop 6.0 mm. of Table II for the two-hour experiments at 393° and 142 cm. initial pressure, shows that about 4.0% of all collisions with the requisite energy are efficient in polymerization. A similar calculation made for the data presented by Pease[7] on the hydrogen-ethylene reaction shows that about 14% of all collisions are efficient.[8] The calculations for ethylene polymerization are, however, of doubtful significance in view of the fact that the reaction is not a simple bimolecular process.

Order of the Reaction

Pease[5] showed that for tank ethylene of "anaesthesia" grade the reaction is second order in the range from 2.5 to 10 atmospheres. He also makes the statement that "at one atmosphere there is some evidence of a fall in rate more rapid than would be expected of a second-order reaction."

Two experiments were made; one at 71 cm. C_2H_4 pressure plus 0.1% C_2H_5SH, and the other with 71 cm. C_2H_4 + 71 cm. CH_4 + 0.1% C_2H_5SH. The temperature was 393°, and the time necessary to obtain the same pressure drop as is obtained at this temperature in two hours at 142 cm. C_2H_4 pressure was found to be exactly eight hours; this would indicate precisely a second-order reaction. However, the yields obtained in these two experiments were 6.5 cc. and 7.5 cc. for the 71-cm. C_2H_4 and the 71-cm. C_2H_4 + 71-cm. CH_4 experiments, respectively. These yields are considerably smaller than the 12.1 cc. obtained in two hours at 142 cm. C_2H_4 pressure. Since the pressure drops were identical, these lower yields indicate that the molecular weight of the products of the 71-cm. C_2H_4 pressure experiments was much higher than for the 142-cm. rate measurement; hence, the percentage of ethylene polymerized must have been much greater in the latter experiments. This conclusion supports Pease's statement that the order at about atmospheric pressure drops faster than would be predicted for a second-order reaction. The somewhat higher yield obtained with 71 cm. C_2H_4 + 71 cm. CH_4 would seem to indicate that although methane helps a little in keeping the rate up it is not very efficient in stabilizing the "hot" molecules of butylene. This fact also shows that if energy chains are present CH_4 is not very efficient in stopping them, for the yield when CH_4 is present is somewhat larger than when CH_4 is absent, whereas one would expect the reverse, namely, a considerably lower yield in the presence of this diluent if gas-phase breaking of energy chains occurred.

Analysis

Reaction Products.—Owing to the relatively small amounts (100 to 150 cc. of gas at normal temperature and pressure) of product available for analysis, no attempt at fractional distillation with controlled reflux was made. Four separations of the Shepherd–Porter type by fractional distillation without reflux were made for each

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(5) A small bulb attached to the mercury valve which closed off the reaction vessel from the rest of the system served as a receiver for the liquefied gases. The mercury valve was lowered until the connection to this bulb was open, and the bulb immersed in a bath of liquid nitrogen.

(6) Pease, This Journal, **53**, 613 (1931).

(7) Pease, *ibid.*, **54**, 1876 (1932).

(8) A calculation made by Vaughan, *ibid.*, **55**, 4115 (1933), is erroneous due to the use of 40,300 cal. as the activation energy instead of 44,000 cal.

olefin. Measurements of gas density made by a magnetic gas-density balance showed that three separations were not sufficient, as 1 to 5% of the olefin one carbon atom lower in the series was present.

Owing to the presence of relatively large amounts of ethyl mercaptan in the C_6 fraction, it was necessary to find a satisfactory method for separating C_2H_5SH and C_6H_{12}. Condensation on a bright surface of metallic sodium was found fairly satisfactory. Experiments made with pure C_2H_5SH showed that at temperatures between 0° and −10° hydrogen and sodium mercaptate were the main products, only a few per cent. of diethyl sulfide being obtained. The analytical data are given in Table III.

TABLE III

ANALYSIS OF REACTION PRODUCTS, PER CENT.

Compound	2-hour experiments	3-hour experiments
Propylene	34.4	39.2
Butylenes	31.4	29.1
Pentenes	29.0	14.4
Hexenes	2.8	14.4
Higher olefins	2.4	2.9
Ratio of propylene to butylene	1.1	1.35

The increase in the C_3H_6/C_4H_8 ratio in the third hour seem to confirm the evidence presented in the first paper[3] concerning the primary product of the reaction. The question is, however, not answered, for even in the two-hour sample corresponding to polymerization of only about 1% of the total ethylene present the fractions of C_3H_6 and C_5H_{10} are of the same order as that of C_4H_8.

Summary

Several methods of preparation of "pure" ethylene were tried in an unsuccessful effort to obtain reproducible rates of polymerization. It was found that the addition of small amounts (about 0.1 per cent.) of ethyl mercaptan to ethylene prepared by fractionation of "anaesthesia grade" tank ethylene, decreased the rate of polymerization about tenfold; and the $C_2H_4 + C_2H_5SH$ mixture polymerized at rates which were reproducible to within about 5%. These rates were in good agreement with the lowest rates obtained in the absence of the mercaptan. The addition of mercaptan did not eliminate the induction period observed in ethylene to which no mercaptan had been added; but did cut down markedly the duration of this induction period. The latter appears to be due to the rate of formation of some intermediate compound which survives freezing to −180° and subsequent revaporization into the reaction chamber at 393°. The polymerization of ethylene is probably not a simple bimolecular reaction. The evidence as to the nature of the primary product is not conclusive but indicates that butylene precedes propylene. The activation energy is 43,500 cal.

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The Partial Molal Volumes of Ammonia and Hydrogen in Liquid Ammonia–Hydrogen Mixtures under Pressure at 100°

BY R. WIEBE AND T. H. TREMEARNE

Ångström[1] measured the change of volume of water and various other organic liquids when hydrogen and other gases were dissolved in them. From his measurements he calculated

$$\Delta V/\Delta V_g = \delta \qquad (1)$$

wherein ΔV_g denotes the volume of gas at standard temperature and pressure dissolved, and ΔV the attending increase in the volume of solvent at constant temperature and pressure. He found that under atmospheric pressure, δ remained constant with varying V_g, Horiuti[2] extended the work of Ångström and confirmed the constancy of δ with concentration in the low pressure region, with sulfur dioxide in various organic liquids an exception.

Upon multiplying both sides of Eq. (1) by V_0, the volume of a mole of the dissolved gas at standard temperature and pressure we obtain $\Delta V/(\Delta V_g/V_0) = \Delta V/\Delta n_2 = V_0\delta$, which leads at once to the relation

$$(\mathrm{d}V/\mathrm{d}n_2)_{P,T} \equiv \bar{v}_2 = V_0 \qquad (2)$$

first stated explicitly by Horiuti[2] (p. 136).

Ångström and Horiuti both worked at low concentrations. At the relatively high concentra-

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[1] Ångström, *Wied. Ann.*, **15**, 297 (1882); *ibid.*, **33**, 223 (1888).

[2] Horiuti, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), No. 341, **17**, 125–256 (1931).