

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WYOMING]

Kinetics of the Thermal Reactions of Ethylene¹BY GEORGE DAHLGREN, JR., AND JOHN E. DOUGLAS²

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Ethylene was pyrolyzed at temperatures from 480 to 582° and at pressures from 0.9 to 13.7 cm. Analyses of the reaction products were made at intervals. Primary products were propene, butene, butadiene and ethane. Propene is formed by a second-order, free radical process which is inhibited by hydrogen sulfide. Possible processes are discussed.

The thermally induced reactions of ethylene, consisting of simultaneous decomposition and polymerization, have been studied for many years. Burk, Baldwin and Whitacre³ review the wide variety of products which have been found. Several workers⁴ have studied the kinetics of the over-all reaction by following the pressure change. Product analyses have been limited and as a result little is known about the way in which product concentrations vary during the course of reaction. The primary products have not been established with certainty, and until they are known the primary processes cannot be established. Of particular interest is the large amount of propene formed under some conditions.⁵

In the study reported here, the course of ethylene pyrolysis has been followed by mass spectrographic analysis with the aim of establishing the primary products and thereby gaining some insight into the processes involved.

Experimental

Ethylene was Phillips research grade (typical lot purity 99.96%) which was further purified by trap to trap distillation with liquid nitrogen. Oxygen could not be detected mass spectrographically in the ethylene thus treated, indicating its concentration to be less than 0.02%. Nitric oxide was obtained from the Matheson Co. with a stated purity of 98.0% and was further purified by trap to trap distillation. Hydrogen sulfide was prepared by the action of 85% phosphoric acid on reagent grade sodium sulfide. The product was dried and fractionated. The reactor was a spherical quartz bulb of 100-cc. capacity, suspended in the center of a vertical, electrically heated tube. The temperature was measured by a thermocouple which could be moved vertically alongside the reactor.

Runs were made statically by allowing the ethylene to expand into the hot reactor from a calibrated volume. The reaction mixture was withdrawn for analysis by allowing it to freeze into a bottle cooled with liquid nitrogen. About one-third of the non-condensables, hydrogen and methane, were collected in this way.

Mass spectral records were obtained with a Consolidated Model 21-103 instrument and were interpreted by using standard patterns from the API collection.⁶ The interpre-

tation was made by starting with the heaviest molecule present, subtracting its contribution to lower masses and proceeding similarly through successively lighter molecules. Such a method is well suited to this situation. The lighter materials, which are of greater interest, are present in greater amount than the heavier materials with which there is a greater chance for ambiguity. The nature of the lighter materials was established in runs of short duration which are free from the complications of heavy products. Since a consistent set of assumptions was carried through all calculations, comparisons are valid even though there may be some error in the absolute magnitudes involved.

Results and Discussion

A. Nature of the Products.—The variety of products found is shown in Table I. Comparison of runs 7 and 8 shows typical reproducibility. Figure 1 shows the variation in product concentration during reaction. For simplicity, products are grouped by carbon number in some cases. It is of interest to note that no acetylene was found in any experiment.

Figures 2 and 3 show, for 582 and 513°, respectively, the percentage of reacted ethylene which is found in the products as reaction proceeds. So that the two plots may be comparable, the abscissa "extent reaction" is used, defined as the per cent. of originally present ethylene which has reacted. Extrapolation to zero reaction shows that the primary products are butene, butadiene, propene and ethane. Although the same primary products are found at both temperatures, their relative concentrations are much different.

The finding of propene to be a primary product is in contradiction to Silcocks'^{4g} conclusion that propene is formed by the reaction of butene with ethylene. This conclusion was based on the constancy of the ratio $(d[C_3H_6]/dt)/[C_4H_8][C_2H_4]$ in the pyrolysis of ethane-ethylene mixtures. However, Silcocks also points out that the ratio $[C_4H_8]/[C_2H_4]$ is a constant. Substitution of the latter ratio into the former gives the results that the ratio $(d[C_3H_6]/dt)/[C_2H_4]^2$ is also a constant. This says that propene is formed with second-order dependence on ethylene, which will be shown below to be the same dependence found in this study. Storch^{4a} concluded that propene was a secondary product from the fact that the ratio $[C_3H_6]/[C_4H_8]$ continued to increase during reaction. Figures 2 and 3 show that the increase in this ratio is due not to increased propene concentration, but rather to a decrease in butene concentration.

A single run was made at initial ethylene pressures of 0.9, 1.4, 3.0 and 7.2 cm., all at 582°. No significant effect was found on either the nature or relative amounts of the products. The addition of nitric oxide (runs 24 and 25, Table I) reduced the amounts of all primary products, especially propene

(1) Abstracted from the M.S. Thesis of George Dahlgren, Jr. The authors gratefully acknowledge the financial support of the Research Corporation and the assistance of the U. S. Bureau of Mines Petroleum and Oil Shale Experiment Station, Laramie, Wyoming, in obtaining mass spectrographic analyses.

(2) Stanford Research Institute, Menlo Park, Calif.

(3) R. E. Burk, B. G. Baldwin and C. H. Whitacre, *Ind. Eng. Chem.*, **29**, 326 (1937).

(4) (a) H. H. Storch, *This Journal*, **56**, 374 (1934); (b) H. H. Storch, *ibid.*, **57**, 2598 (1935); (c) R. N. Pease, *ibid.*, **52**, 1158 (1930); (d) R. N. Pease, *ibid.*, **53**, 613 (1931); (e) H. D. Burnham and R. N. Pease, *ibid.*, **64**, 1404 (1942); (f) M. J. Mclera and F. J. Stubbs, *J. Chem. Soc.*, 881 (1952); (g) C. G. Silcocks, *Proc. Roy. Soc. (London)*, **A233**, 465 (1955).

(5) (a) J. E. Douglas, B. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955); (b) F. E. Frey and D. F. Smith, *Ind. Eng. Chem.*, **20**, 948 (1928); (c) S. Lenher, *This Journal*, **53**, 3752 (1931).

(6) American Petroleum Institute, Research Project 44, Carnegie Institute of Technology, Catalog of Mass Spectral Data.

TABLE I
 RESULTS OF SELECTED RUNS

Run no.	14	24	26	28	7	8	25	27	29
Addend	None	5% NO	7% H ₂ S	2% O ₂	None	None	5% NO	7% H ₂ S	2% O ₂
Initial press. C ₂ H ₄ (cm.)	13.4	14.2	14.4	14.8	13.7	13.7	14.0	13.6	14.1
Temp. (°C.)	583.4	579.5	579.9	579.8	580.4	580.4	580.1	579.9	580.0
Time (min.)	10	10	10	10	45	45	45	45	45
Extent reaction	5.8	1.1	7.1	28.7	26.0	28.0	18.4	24.8	39.6
Products ^a									
Toluene	<2.0	...	2.0	2.0	2.8	3.1	1.1	1.0	1.2
Cyclohexene	<2.0	1.2	1.0
Cyclohexadiene	<2.0	1.1
Benzene	5.2	...	22.0	12.2	25.5	25.4	11.8	24.2	12.1
Pentene	...	2	2.0	2.5	1.0	0.5	2.5	1.2	1.5
Cyclopentene	6.8	1.7	2.1	1.1	2.5	...	1.2
Cyclopentadiene	8.5	...	3.2	3.9	3.6	...	5.2	0.9	2.7
Butene	12.3	32	8.2	4.3	3.9	3.4	5.9	2.6	2.5
Butadiene	11.6	14	9.0	3.4	2.8	1.6	4.5	2.4	1.9
Propane	4.3	42	5.7	1.6	0.9	1.7	1.7	2.0	1.9
Propene	28.8	...	4.0	12.4	25.0	21.2	26.0	4.2	13.3
Ethane	15.1	10	36.8	20.2	2.4	22.4	15.2	36.5	29.0
Methane	7.2	...	7.1	34.1	30.1	19.6	22.7	25.0	32.4
Hydrogen	190	35.4	30.2	44.2	56.5	26.8

^a Expressed as per cent. reacted ethylene in products, except for hydrogen which is expressed as 100 × moles hydrogen formed/moles ethylene reacted. Values for methane and hydrogen are approximate only due to uncertainty in fraction collected (see text).

and ethane. This implies that free radical processes are involved in forming these substances.

Addition of hydrogen sulfide (runs 26 and 27, Table I) markedly reduced propene formation, increased ethane and had little effect on other products. Hydrogen sulfide was investigated because of Storch's finding^{4a} that addition of ethyl mercaptan to pyrolyzing ethylene brought the rate into agreement with his most highly purified, oxygen-free ethylene.⁷ The hydrogen sulfide may be re-

the surface area showed no significant variation from similar runs in an unpacked reactor.

B. Kinetic Data.—The order of reaction for over-all ethylene removal was determined at 513 and 582° by plotting the appropriate concentration functions *vs.* time for several integral and half orders. The best straight line was obtained from the second-order rate equation. There was indication of a short induction period. The second-

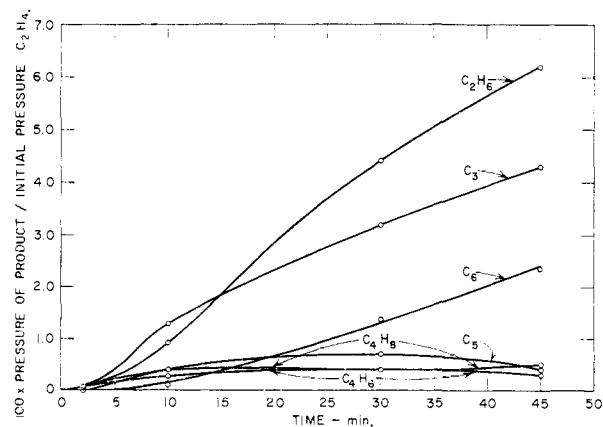


Fig. 1.—Products as a function of time: temp. 582°, press. 13.7 cm.

moving radicals important in propene formation through reactions of the type $R + H_2S \rightarrow RH + HS$. Two runs made with added oxygen showed an increase in ethane and propene in early stages of reaction. Two runs in which the reactor was packed with quartz needles so as to about double

(7) Since ethyl mercaptan rapidly decomposes into ethylene and hydrogen sulfide at these temperatures (N. R. Trenner and H. S. Taylor, *J. Chem. Phys.*, **1**, 77 (1933)), it is likely that the effect observed by Storch was due to hydrogen sulfide rather than to the mercaptan.

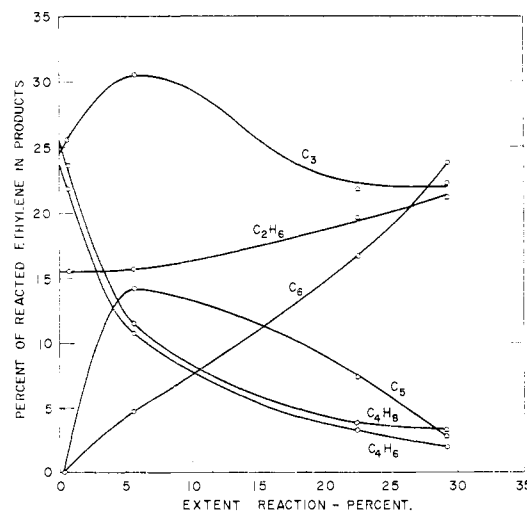


Fig. 2.—Products, expressed percentagewise, as a function of extent of reaction: temp. 582°, press. 13.7 cm.

order rate law was confirmed at 582° by comparison of the results at 13.7 cm. pressure with those at three lower pressures using the fractional period method. Propene formation was found also to be second order from a similar fractional period calculation. Since it is likely that C₅ and C₇ products are formed by reaction of propene with additional

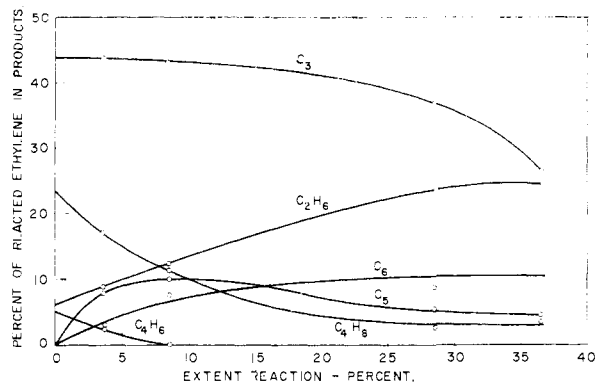


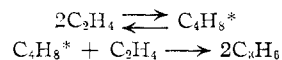
Fig. 3.—Products, expressed percentagewise, as a function of extent of reaction: temp. 513°, press. 13.7 cm

ethylene, total propene formation was taken as the sum of C₃ plus C₅ plus C₇ products in this calculation.

Second-order rate constants for over-all ethylene removal were calculated from the slopes of the appropriate concentration *vs.* time plot. At 582° $k = 6.3 \times 10^{-2}$ liter mole⁻¹ sec.⁻¹; at 513° $k = 7.6 \times 10^{-3}$ liter mole⁻¹ sec.⁻¹. These rate constants give an activation energy of 41.1 kcal. mole⁻¹. A rate constant of 1.4×10^{-3} liter mole⁻¹ sec.⁻¹ was calculated for 482° on the basis of a single run with the assumption that the line passes through the origin.

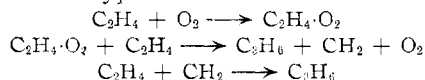
C. Mechanism. Propene.—The preceding discussion has shown that propene is formed in a process that does not require the build up of stable intermediates, is second order in ethylene, involves free radicals and may possibly involve catalysis by traces of oxygen. It is worthwhile to discuss the possible processes which are compatible with these requirements. Acetylene has been mentioned as an intermediate in ethylene pyrolysis at higher tem-

peratures.⁸ However, it seems unlikely that it is important under the conditions of these experiments since none was found in the products and since it is unlikely that there is rupture of the C≡C bond. Other processes which require fragment formation by carbon-carbon bond rupture seem unlikely since quite long chains would be required. A possible process is



The excited C₄H₈* molecule may be a diradical; if so, this could account for the observed inhibition of propene formation by both nitric oxide and hydrogen sulfide.

It is possible that rupture of the carbon-carbon bond may be facilitated by traces of oxygen, as suggested by the hydrogen sulfide inhibition. A process of this type is



The species C₂H₄·O₂ could be a peroxide as suggested by Lenher^{9c} or a loosely bound complex. Since the oxygen is regenerated, trace quantities are capable of causing many reaction cycles.

Butadiene and Ethane.—Butadiene does not arise from the dehydrogenation of butene since the butadiene forms at once, before butene build-up. Nor does butadiene arise from the same activated state as butene since the temperature dependence is different for the two substances. A possible process is C₄H₈* + C₂H₄ → C₄H₆ + C₂H₆. This implies that each should have the same initial rate of formation. The data, although not conclusive, indicate that this may be so.

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