[CONTRIBUTION FROM THE CHEMICAL LABORATORY, PRINCETON, UNIVERSITY]

THE NON-CATALYTIC POLYMERIZATION AND HYDROGENATION OF ETHYLENE[1]

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RECEIVED OCTOBER 22, 1929 PUBLISHED MARCH 6, 1930

There is now ample evidence that the only primary reaction involved in the vapor-phase cracking of the gaseous saturated aliphatic hydrocarbons (excepting methane) up to at least 650° and in the absence of catalysts is a homogeneous unimolecular dissociation yielding mono-olefins and saturated hydrocarbons of lower molecular weight, or hydrogen. The products of this primary action may, however, suffer further change. The lower hydrocarbons may themselves dissociate. The olefins may polymerize or dissociate. They may also react with any hydrogen which has been formed. The so-called "pyrolysis" of the original hydrocarbon may therefore yield a complex of products. As a further step in the unravelling of the chemical changes involved in this process, some investigation of the behavior of olefins is called for. In this connection we have undertaken a preliminary study of the thermal reactions of ethylene, the results of which are here reported.

Method.—Experiments were conducted mainly by the flow method at atmospheric pressure, though one series of static determinations was carried out. The gases—ethylene, hydrogen and nitrogen, all of high purity—passed through resistance-tube flowmeters and calcium chloride tubes into a pyrex reaction tube which was heated in an electric tube-furnace. The off-gas was collected over mercury and analyzed for higher olefins by absorption in ordinary concentrated sulfuric acid, for ethylene by absorption in dilute bromine water, and for hydrogen and saturated hydrocarbons by fractional combustion with copper oxide. Qualitative tests for acetylene were conducted with ammoniacal cuprous chloride, and showed at most the barest traces of this gas under any conditions studied.

Results

Ethylene Alone.—The behavior of pure ethylene at 1 atm. was investigated by the flow method between 450 and 600°. Data are presented in Table I. The results indicate that the only important reaction at the lower temperatures is the formation of a butylene

$$2C_2H_4 \longrightarrow C_4H_8$$

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[1] This paper contains the results of an investigation carried out as part of Project No. 7 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund donated by Mr. John D. Rockefeller. This fund is being administered by the American Petroleum Institute with the coöperation of the Central Petroleum Committee of the National Research Council. Professor Hugh S. Taylor of Princeton University is Director of Project No. 7.

This conclusion is based on the fact that one volume of gas absorbable by ordinary concentrated sulfuric acid is formed for every two volumes of ethylene disappearing. Above 525°, ethane, methane, a little hydrogen and liquid products begin to appear. The formation of ethane is about in proportion to the amount of ethylene reacting, and this substance is consequently regarded as a primary product. Its amount is never large, and passes through a maximum at 575–600°. Methane is formed at an increasing rate as the heating time is increased, which suggests that it is a secondary product. These data are in general agreement with those of Day,[2] of Hague and Wheeler[3] and of Frey and Smith.[4]

TABLE I

REACTION OF ETHYLENE AT 450–600° AND 1 ATM.

Reaction-tube volume, 637 cc.

Temp., °C.	Gas flow, cc./min.	C_2H_4, cc. In	Out	Reacted	Formed, cc. "C_nH_{2n}"	C_2H_6	CH_4	H_2
450	40	100	95	5	2	2	2	2
	20	100	93	7	3	1	1	1
	10	100	90	10	4	2	2	2
	5	100	85	15	7	1	1	1
475	40	100	94	6	3	1	1	1
	20	100	90	10	4	1	1	1
	10	100	86	14	6	1	1	1
	5	100	78	22	9	3	3	3
500	40	100	92	8	4	2	2	2
	20	100	86	14	6	2	2	2
	10	100	81	19	8	4	4	4
525	40	100	91	9	4	1	1	1
	20	100	83	17	7	3	3	3
	10	100	72	28	9	7	7	7
550	40	100	83	17	6	4	1	1
	20	100	72	28	8	5	4	1
	10	100	58	42	9	8	7	2
575	40	100	77	23	7	6	2	1
	20	100	60	40	9	10	6	2
	10	100	48	52	7	12	13	3
600	40	100	66	34	7	5	9	2
	20	100	53	47	7	9	12	3
	10	100	40	60	7	11	22	3

The kinetics of the low temperature reaction are peculiar. The flow experiments show that the rate falls off rapidly as the heating time is increased (*i. e.*, the flow-rate is decreased) and the temperature coefficient is rather small. These might be characteristics of a contact action occurring at the reaction tube walls. To test this point, experiments by the static

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[2] Day, *Am. Chem. J.*, **8**, 153 (1886).

[3] Hague and Wheeler, *J. Chem. Soc.*, 391 (1929).

[4] Frey and Smith, *Ind. Eng. Chem.*, **20**, 948 (1928).

method (pressure decrease at constant volume) were carried out by Mr. Paul R. Chesebro. Rates in an empty pyrex tube were compared with rates in a tube packed with broken pyrex glass. If a wall reaction were occurring, the rates in the packed tube would be the greater. Actually the pressure drop was definitely more rapid in the empty tube. Data are given in Table II.

TABLE II

STATIC EXPERIMENTS IN EMPTY AND PACKED PYREX BULB

Temp., °C.	Time, min.	Pressure, mm.	ΔP per 10 min.	Pressure, mm.	ΔP per 10 min.
		Empty Bulb		Packed Bulb	
400	0	746	4	775	3
	10	742	4	772	3
	20	738	4	769	4
	30	734	3	765	2
	40	731	4	763	2
	50	727	3	761	1
	60	724		760	
450	0	799	19	788	14
	10	780	12	774	6
	20	768	9	768	7
	30	759	10	761	5
	40	749	7	756	6
	50	742	8	750	6
	60	734		744	
500	0	788	36	775	23
	10	752	24	752	12
	20	728	19	740	11
	30	709	18	729	10
	40	691	13	719	10
	50	678	11	709	11
	60	667		698	

Wall material has therefore a depressing action on the reaction. Similar though more marked effects have been observed in the oxidation of hydrogen[5] and of hydrocarbons,[6] and have been attributed to the occurrence of a homogeneous chain-type reaction in the empty tube, which reaction is suppressed by the packing. A similar explanation will serve in the case of ethylene. Since the effect is not great, it is concluded that either the glass is relatively inefficient in the case of ethylene or that the chains are not long (*i. e.*, chain propagation is not efficient). There is, however, no question but that a negative surface action predominates.

Further evidence of the unusual nature of the reaction was obtained from a set of static experiments carried out in the empty bulb. These are summarized in Table III.

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[5] Hinshelwood and Thompson, *Proc. Roy. Soc. London,* **118A,** 170 (1928).

[6] Pease, THIS JOURNAL, **51,** 1839 (1929).

TABLE III

STATIC EXPERIMENTS AT 400, 450 AND 500° (EMPTY BULB)

Temp., °C.	Time, min.	Pressure, mm.	ΔP per 10 min.	Pressure, mm.	ΔP per 10 min.	Pressure, mm.	ΔP per 10 min.
400	0	602	4	746	4	899	9
	10	598	3	742	4	890	8
	20	595	3	738	4	882	6
	30	592	2	734	3	876	4
	40	590	3	731	4	872	4
	50	587	3	727	3	868	3
	60	584		724		865	
450	0	588	5	799	19	901	22
	10	583	6	780	12	879	17
	20	577	4	768	9	862	12
	30	573	5	759	10	850	10
	40	568	4	749	7	840	9
	50	564	5	742	8	831	9
	60	559		734		822	
500	0	582	15	788	36	910	40
	10	567	12	752	24	870	26
	20	555	9	728	19	844	21
	30	546	8	709	18	823	19
	40	538	8	691	13	804	16
	50	530	6	678	11	788	15
	60	524		667		773	

It will be noted that the reaction rate is initially high in certain of the experiments. The indication is that for this initial high rate to appear, a certain minimum initial pressure is required, this pressure being the lower the higher the temperature. Thus at 400° it is between 750 and 900 mm., at 450° it is between 590 and 800 mm., at 500° it is less than 580 mm. A far more pronounced minimum pressure effect has been observed in the oxidation of phosphorus vapor by Semenoff.[7] In the latter case there is no reaction whatever below a given low pressure but instantaneous reaction above, and temperature changes do not affect the results. This behavior was attributed to the occurrence of a chain reaction. The data on ethylene may perhaps indicate a residual influence of this same nature.

Further evidence of the influence of pressure may be seen in the results of flow experiments in which ethylene was diluted with nitrogen. These will be found in Table IV. These experiments—at 575°—would have indicated that the reaction was roughly bimolecular.

There is no question but that the kinetics of the ethylene condensation are out of the ordinary. It is probable that molecular excitation and chain reaction play important roles, but the precise nature of the reaction is not clear. Combustion data indicate that the change

$$2C_2H_4 \longrightarrow C_4H_8$$

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[7] Semenoff, *Z. Physik*, **46**, 109 (1927).

is mildly exothermic, evolving about 17,000 cal. This, plus the original energy of activation, is to be regarded as the source of the excitation energy.

It appears that two molecules of ethylene may combine to give an excited molecule of butylene. This may subsequently become de-activated without any other effect; or it may excite a fresh ethylene molecule under favorable conditions of pressure and temperature; or, finally, it may react with a fresh ethylene molecule, producing ethane and a residue which subsequently appears in the liquid product. A more complete interpretation of the reaction must await further investigation.

Ethylene–Hydrogen.—Ethylene and hydrogen combine to form ethane in the neighborhood of 600°, the reaction being reversible but nearly complete at this temperature.[8] The reaction is of especial interest in connection with the ethylene condensation already discussed because the two must compete in some manner. Flow experiments were carried

TABLE IV

BEHAVIOR OF ETHYLENE–HYDROGEN–NITROGEN MIXTURES AT 550, 575 AND 600°

Reaction tube volume 637 cc.; total gas flow rate, 40 cc./min.

Temp., °C.	Gas in, cc.			Reacted, cc.		Formed, cc.		
	C_2H_4	H_2	N_2	C_2H_4	H_2	C_2H_6	CH_4	"C_nH_{2n}"
				50% Ethylene–Nitrogen				
550	50	0	50	5	..	2	0	2
575	50	0	50	8	..	3	0	2
600	50	0	50	11	..	5	2	4
				50% Ethylene–Hydrogen				
550	50	50	0	10	9	7	0	2
575	50	50	0	14	11	11	0	2
600	50	50	0	21	16	14	4	1
				100% Ethylene				
550	100	0	0	17	..	4	1	6
575	100	0	0	23	..	6	2	7
600	100	0	0	34	..	5	9	7
				Ethylene–Nitrogen				
575	25	0	75	2	..	0	1	1
575	50	0	50	8	..	0	3	2
575	75	0	25	13	..	0	3	4
575	100	0	0	23	..	2	6	7
				Ethylene–Hydrogen				
575	25	0	75	2	..	0	1	1
575	25	25	50	6	3	4	0	0
575	25	50	25	10	8	9	1	0
575	25	75	0	17	15	15	1	0

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[8] Pease and Durgan, THIS JOURNAL, 50, 2715 (1928).

out at 550, 575 and 600° to determine the nature of the result of this competition. Data are given in Table IV.

The first three sections of Table IV give results for a 50% ethylene–nitrogen mixture, for a 50% ethylene–hydrogen mixture and for pure ethylene, each at 1 atm. and at 550, 575 and 600°. An inspection of these results makes it quite clear that hydrogenation does not occur independent of condensation. It is true that twice as much ethylene reacts in the presence of hydrogen as in the presence of nitrogen, but in the former case nearly the whole of the ethylene is hydrogenated and not merely the excess over that reacting in presence of nitrogen. Further, the product is definitely ethane and not butane, as might have been the case had butylene first been formed and then immediately hydrogenated. Again, it will be noted that the temperature coefficient of reaction rate is the same for ethylene diluted with nitrogen and for ethylene diluted with hydrogen. Finally, it may be pointed out that the sum of the ethylene and hydrogen reacting in the 50% mixture is nearly equal to the total of ethylene reacting when this substance is taken alone at 1 atm. The numbers are 19, 25 and 37 cc. for ethylene plus hydrogen, and 17, 23 and 34 cc. for ethylene alone at the three temperatures. Given half an atmosphere of ethylene, it makes little difference so far as total rate is concerned whether one adds half an atmosphere of ethylene or of hydrogen. Actually it does make some difference, hydrogen being more effective than ethylene. Thus, if we start with $^1/_4$ atm. of ethylene diluted with $^3/_4$ atm. of nitrogen, and add ethylene in one case and hydrogen on the other, we obtain the results given in the fourth and fifth sections of Table IV. The total gas reacting in a mixture of $25C_2H_4$–$75H_2$ is nearly half again as great as in pure ethylene. For total pressures of $^1/_2$, $^3/_4$ and 1 atm. at 575°, the figures for ethylene alone are 8, 13 and 23 cc. For ethylene–hydrogen mixtures they are 9, 18 and 32 cc. In the latter case, with constant ethylene concentration, the rate increases much more rapidly than the hydrogen concentration. Taking everything into consideration, it would appear that the hydrogen activates the ethylene for subsequent reaction with itself (hydrogen). Similar evidence as to the hydrogenation reaction is to be found in the work of Frey and Smith.[4]

In introducing this section of the investigation it was suggested that the hydrogenation and condensation reactions must compete. This appears to be true in the sense that the two compete for active ethylene. In absence of hydrogen this forms butylene and the other products of the condensation reaction. In presence of hydrogen it forms chiefly ethane. In addition it is not improbable that hydrogen is capable of accelerating the production of active ethylene.

It is evident that experiments at higher pressures should yield significant data regarding these reactions. It is planned to carry these out shortly.

Summary

The non-catalytic polymerization and hydrogenation of ethylene has been studied, the former between 450 and 600° and the latter between 550 and 600°. The polymerization reaction probably first produces butylene. It gives evidence of being of the chain type, and is certainly not conventional in its mechanism. The hydrogenation reaction appears to be closely coupled with the polymerization. Its rate is of the same order. Ethylene which would have polymerized is largely converted to ethane in presence of hydrogen.

PRINCETON, NEW JERSEY

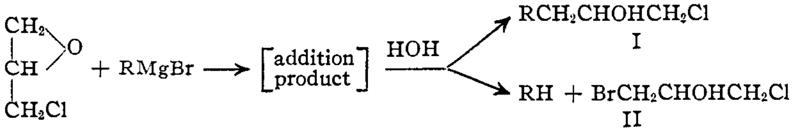
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE REACTION OF VARIOUS GRIGNARD REAGENTS WITH EPICHLOROHYDRIN. THE PREPARATION OF SOME NEW CHLOROHYDRINS

BY C. FREDERICK KOELSCH AND S. M. McELVAIN

RECEIVED OCTOBER 28, 1929 PUBLISHED MARCH 6, 1930

The reaction between epichlorohydrin and various Grignard reagents has been studied by Fourneau and Tiffeneau.[1] These investigators reported that they were unable to isolate any product formed by the development of a new carbon to carbon linkage when Grignard reagents derived from ethyl, propyl, butyl or amyl bromides were allowed to react with epichlorohydrin; in all cases the sole products obtained were the hydrocarbons formed by the hydrolysis of the Grignard reagent used, and glycerol chlorobromohydrin. However, when phenyl-, benzyl- or *p*-anisylmagnesium bromide was allowed to react with epichlorohydrin, they found that an appreciable yield of a chlorohydrin with a structure (I) could be isolated along with the hydrocarbon and glycerol chlorobromohydrin (II). These reactions may be indicated thus



In a previous paper[2] from this Laboratory it was shown that it was possible to isolate a chlorohydrin with the structure of I from the reaction of ethylmagnesium bromide and epichlorohydrin. Since this result was so different from that obtained by Fourneau and Tiffeneau, it seemed advisable to extend the study of the reaction to some of the higher alkyl

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[1] Fourneau and Tiffeneau, *Bull. soc. chim.*, [4] **1**, 1227 (1907).

[2] Koelsch and McElvain, THIS JOURNAL, **51**, 3390 (1929).