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THE CATALYTIC COMBINATION OF ETHYLENE AND HYDROGEN IN THE PRESENCE OF METALLIC COPPER. I. MEASUREMENTS OF REACTION VELOCITY AND ADSORPTION ISOTHERMS AT 0° AND 20°

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Received February 19, 1923

Ever since the time of Faraday it has been conjectured that in many contact catalytic actions, surface condensation, or as we should say now, adsorption of the reacting substances by the contact material plays an important role. So far as the writer is aware, however, a comprehensive investigation of the characteristics of a particular contact action on the one hand and of the adsorption of the reactants and products by the contact material on the other has not been carried out. This has been the object of the present research.

The combination of ethylene and hydrogen in the presence of metallic copper has been chosen as a suitable reaction for investigation. This reaction appeared to have the practical advantages (1) that reactants and product are gaseous and reasonably stable, (2) that reaction goes to practical completion, (3) that there is no possibility of interaction with the catalyst or of side reactions, (4) that the reaction takes place at moderate temperatures—from 150° up, according to Sabatier[1]—and (5) that its course is easily followed, since it occurs with decrease of pressure at constant volume. It was known from the work of Grassi[2] that at temperatures between 150° and 300° the reaction was normal (bimolecular), at least in its first stages, which were all that Grassi investigated; and from the work of Taylor and Burns[3] it was known that catalytically active copper adsorbed ethylene strongly at low temperatures, though apparently it did not adsorb hydrogen in anything like as great amounts, and it adsorbed neither gas in the temperature region in which the catalytic action was supposed to take place. In addition, the reaction chosen is in itself of special interest because it is the simplest example of the hydrogenation of the double bond, the reaction involved in the catalytic hydrogenation of oils.

Because of the known variability among samples of catalytically active material both as regards catalytic activity and adsorptive capacity, it was considered vital to obtain measurements of the two properties on

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[1] Sabatier, "La Catalyse en Chimie Organique," Librairie Polytechnique, Paris, 2nd ed., **1920**, p. 193.

[2] Grassi, *Il Nuovo Cimento*, [6] 11, 147 (1916).

[3] Taylor and Burns, THIS JOURNAL, **43,** 1273 (1921).

the same sample of material. This has accordingly been done. Measurements of reaction velocity have been alternated with determinations of adsorption isotherms on the same sample of catalyst in such a way that sets of measurements of each kind have been "bracketed" by measurements of the other. This has been done in order to take account of any change in activity.

Apparatus and Procedure

The apparatus used is pictured in Fig. 1. Its essential parts are the catalyst bulb, A, the mercury manometer, B, the gas buret, C, and a Töpler pump. These were all connected by glass seals. The catalyst bulb was about 10 cm. long by 2.5 cm. in diameter and contained usually about 100 g. of copper. The catalyst was prepared in place in the bulb. Before being sealed to the apparatus, the bulb was filled with copper oxide granules of about 10–20 mesh through a wide tube sealed on at the bottom. This tube was then drawn down but not sealed off and the bulb connected in place. The bulb was then raised to a temperature of 200° in an electrically heated air-bath while electrolytic hydrogen was passed through it at a rate of 25 cc. per minute. Reduction usually required 30–40 hours under these conditions with a sample of copper oxide weighing about 120 g., and was considered complete when passage of the effluent hydrogen through a calcium chloride tube caused no gain in weight of the latter. With the hydrogen still flowing, the bulb was cooled to room temperature and the outlet tube sealed off where it had already been drawn down. There was in all cases some shrinkage in volume on reduction of the oxide, amounting to 5 to 10%.

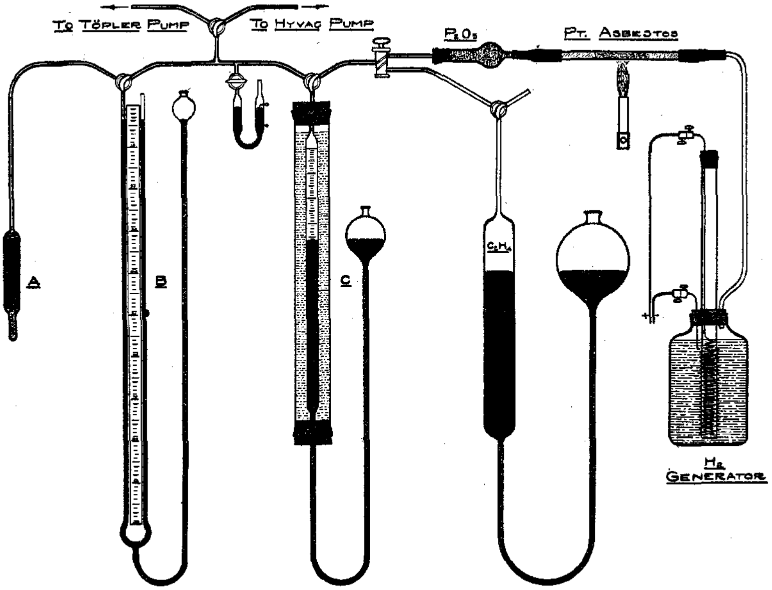

Fig. 1.—Apparatus.

The gas buret contained mercury as retaining liquid; it was equipped with a small manometer which was used in adjusting the pressure inside the buret, and was calibrated with mercury before being used. It could be read to about 0.03 cc. Quantities of gas are expressed throughout in volumes reduced to 0° and 760 mm., assuming the gas laws to hold.

The scale of the manometer was of wood and was compared with a steel scale before use. Within the limit to which it could be read, namely 0.2 mm., it was satisfactory. All manometer readings were reduced to 0°

The hydrogen used in the experiments was generated electrolytically between nickel wire electrodes in a cell containing caustic soda solution. It was passed over red hot palladized asbestos to remove oxygen and then through phosphorus pentoxide to dry it. Hydrogen was generated as required and run directly into the buret.

C. P. compressed ethylene was purified by passing it through calcium chloride and a tube immersed in a mixture of solid carbon dioxide and ether to remove condensible impurities. The gas so treated was 99.5% absorbed by fuming sulfuric acid. Ethylene prepared from alcohol and phosphoric acid and from ethylene dibromide and zinc was also used in some of the earlier experiments. No difference in behavior was noted and the purity of these prepared gases was no greater than that of the commercial gas.

The ethane used in adsorption experiments was prepared by allowing carefully prepared 50% mixtures of ethylene and hydrogen to react to completion in the catalyst bulb. The product was then pumped off and stored in a collecting buret over mercury.

The measurements of reaction velocity were carried out as follows. The required volumes of hydrogen and ethylene were drawn into the buret and were then mixed by repeated compression and expansion. A Dewar vessel containing a water-ice mixture was raised to surround the catalyst bulb, which had been previously evacuated at 200°. After the bulb had been in the cooling mixture for 1–1.5 hours, the gas mixture was admitted, the bulb immediately connected to the manometer and pressure readings were taken every minute, in the case of the active catalysts, and every 5 minutes, in the case of the less active material. When reaction was complete, the Dewar vessel was replaced by the electrically heated air-bath and the temperature raised to 200° while the bulb was pumped out. After that temperature was reached and the volumes of gas given off had become small, the Töpler pump was operated once every 5 minutes until less than 5 cu. mm. of gas was obtained at one stroke. This usually required from 40 minutes to 1 hour. The bulb was then allowed to cool to room temperature, when it was ready for another experiment.

In an adsorption experiment, the buret was filled and the catalyst bulb brought to temperature as above. Gas was then admitted to the bulb in small quantities and pressure readings were taken after each addition until 3 successive readings at 5-minute intervals did not vary within the limit to which readings could be made, namely, 0.2 mm. Pressures corresponding to 6–10 additions of gas were taken in each run. The quantities of gas adsorbed were calculated from the volume of gas required to fill the bulb at a given pressure and the volume of helium required to give the same pressure. It was assumed that no helium was adsorbed.

The contact material prepared as described above was much more active both as to its catalytic activity and as to its adsorptive capacity than previous investigators have reported. Thus, according to both Sabatier and Grassi, reaction only commences at about 150° whereas this material caused practically instantaneous reaction at this temperature, and reaction in 40–50 minutes' time at 0°, starting with a mixture of 0.5 atmosphere each of ethylene and hydrogen. As to adsorptive capacity, Taylor and Burns report the equivalent of less than 0.2 cc. of hydrogen and of 2.85 cc. of ethylene per 100 g. of copper at 25° and 1 atmosphere, while the writer found 3 cc. of hydrogen and 8 cc. of ethylene at 0°. (The adsorptions do not change greatly between 0° and 25°.) Although this catalyst was rather unsatisfactory for use in accurate velocity measurements a series of experiments was carried out with it in order that a rough comparison might be made with a less active material. These results will be referred to later. It was suspected that the activity of the catalyst could be reduced by heating it to moderately high temperatures. This was found to be the case. Prior to its use in the experiments mentioned above, the catalyst had been heated to 300° for 1.5 hours and had not since then been above 200°. When this was heated to 350° in a vacuum for an hour and then to 400° for an hour no marked change in activity was caused. Finally, it was heated to 450° for 1.5 hours, after which the activity was found to be about $^1/_7$ its former value. The catalyst in this state was used in the subsequent experiments. The results of this series will be presented first, after which some of the results with the more active material will be given. It may be stated at the outset that the two sets of results differ only in degree.

Treatment of Results.—It has not seemed advisable to attempt to present a detailed analysis of the results of the velocity measurements at this time because of the probability that the change in pressure in a given experiment as reaction proceeds is not entirely due to the decrease consequent on the formation of a molecule of ethane from a molecule each of ethylene and hydrogen, but depends as well on the change in the total amount of the gases adsorbed with changing partial pressures. There is evidence that at the beginning of a run the total amount of gas adsorbed is equal to the amount of ethylene alone that one would expect to be adsorbed at its partial pressure; for the initial pressure in a velocity measurement, obtained by extrapolation to zero time, is about equal to the sum of the pressure that the ethylene would exert if it were alone present in the bulb and the pressure that the hydrogen would exert if it were not adsorbed at all and were exerting the same pressure as an equal amount of helium. This may mean that in presence of ethylene, hydrogen is actually not adsorbed at all or that any hydrogen adsorbed simply

TABLE I

COMPARISON OF CALCULATED AND EXTRAPOLATED INITIAL PRESSURES

Partial pressures			
H_2[a] Mm. Hg	C_2H_4[b] Mm. Hg	Calc. total pressure Mm. Hg	Extrapolated pressure Mm. Hg
422	342	762	759
201	144	345	349
416	338	754	757
420	341	761	764
216	158	374	380
280	468	748	750
140	214	354	359
547	210	757	757
277	92	369	374
421	341	762	762
423	342	765	766
421	341	762	765
		Av. 626	Av. 628

[a] "Helium value."

[b] From adsorption isotherm.

displaces an equal quantity of ethylene on the surface. The latter seems to the writer the more probable. The evidence is based in the preceding table, which refers to measurements on the de-activated catalyst at 0°.

One might assume, therefore, that so far as ethylene and hydrogen are concerned the total amounts adsorbed are equal to the amount of ethylene adsorbed when it alone is present in the quantity in which it is present in the mixture. This leaves the adsorption of ethane out of account, however. Since the change in adsorption of ethane at low pressures and of ethylene at high pressures is about the same, one might further assume that during the first stages of an experiment the ethane formed compensated for the ethylene which has reacted, so far as adsorption is concerned. These two assumptions taken together would mean that the total amount of gas adsorbed remained constant and that therefore the change in pressure was entirely due to reaction and was a direct measure of reaction rate. Making these assumptions, velocity constants may be calculated with the result that in any given run fairly good constants are obtained for a reaction *unimolecular with respect to hydrogen,* assuming that the total amount of hydrogen present constitutes its active mass. Moreover, the constants for those runs in which the initial total pressure was 1 atmosphere agree among themselves, as do those in which the initial total pressure is 0.5 atmosphere, but the latter constants are nearly twice the former. In view of the somewhat doubtful nature of the necessary assumptions and the difficulty of accounting for the results just cited, it has seemed better to analyze the measurements in a different manner. It has been assumed that the decrease in pressure from the 5th to the 15th minute is entirely due to reaction and can be compared in different runs with the initial quantities of ethylene and hydrogen admitted to the bulb. From such comparisons, the influence of concentration of ethylene and hydrogen on reaction velocity, as measured by this decrease in pressure, has been calculated.

Results of Measurements

The results of the velocity and adsorption measurements have been brought together in Table II.

In the velocity measurements, the pressures at zero time were obtained by extrapolation of readings taken every minute during the first 10 minutes. The final pressure (at $t = \infty$) is given in the case of the measurements with 50% mixtures and represents the pressure which the equivalent quantity of ethane would exert, as determined by the adsorption measurements.

The values for adsorption were obtained by plotting the results and interpolating for even pressures.

Discussion of Measurements at 0°.—By way of illustration, curves for the velocity and adsorption measurements with the de-activated cata-

TABLE II

VELOCITY MEASUREMENTS

	Before de-activation		After de-activation										
	At 0°		at 0°							At 20°			At 0°
Expt.	50	53	62	63	64	65	66	67	68	78	79	80	81
H_2, cc.	27.35	27.25	26.00	13.35	17.30	8.65	33.80	17.15	26.00	23.85	31.35	16.00	26.05
C_2H_4, cc.	27.45	27.25	26.05	13.40	34.55	17.25	16.95	8.60	26.00	23.85	15.65	32.10	26.05
Time min.	Pressure, mm. Hg				Pressure, mm. Hg					Pressure mm. Hg			Pressure mm. Hg
0	(773)	(767)	(764)	(380)	(750)	(359)	(757)	(374)	(762)	(761)	(761)	(760)	(765)
5	630	630	745	364	737	347	731	354	741	702.5	689.5	712	747
10	521	520	730.5	351.5	727.5	339.5	709	338	725	652.5	629	676	737
15	443	442	717	340	719	332.5	688	323.5	710	610	576	645.5	722.5
20	395	395	704	328.5	710.5	325.5	668	310.5	695.5	573	534.5	618.5	711
25	376	374	691	...	703	...	648	298.5	681	540	512	596.5	700
30	372	370	679	308.5	695.5	313.5	629.5	287.5	667	511.5	511	576	689.5
60	...	...	611.5	257	654.5	282.5	532.5	264	...	405.5	509.5	508	632.5
90	...	...	...	222	...	258.5	489	...	...	383.5	...	487.5	...
180	...	...	443.5	...	547.5	...	...	...	...	...	...	...	...
300	...	...	385	...	498	...	...	...	...	...	...	...	...
∞	...	...	370	187	...	...	...	...	370	...	...	...	...

ADSORPTION MEASUREMENTS

	Before de-activation			After de-activation											
	At 0°			At 0°								At 20°			
Expt.		51	52		57	71	Av.	58	70	Av.	56		77	76	75
	Helium	H_2	C_2H_4	Helium	Hydrogen			Ethylene			Ethane	Helium	H_2	C_2H_4	C_2H_6
Pressure mm. Hg	value Cc.	Cc. Gas adsorbed		value Cc.	Cc. Gas adsorbed							value Cc.	Cc. Gas adsorbed		
10	0.65	1.75	2.45	0.65	0.35	0.30	0.33	1.45	1.45	1.45	0.15	0.60	0.45	1.05	0.05
50	3.10	2.30	3.55	3.10	.55	.50	.53	2.40	2.35	2.38	.53	2.90	.50	1.67	.20
100	6.20	2.60	4.50	6.20	.80	.70	.75	3.05	3.00	3.03	1.02	5.80	.60	2.20	.45
200	12.40	3.05	5.55	12.40	.90	.75	.83	3.95	3.85	3.90	1.85	11.55	.70	2.85	.92
380	23.50	3.35	6.85	23.50	1.05	.90	.98	5.20	5.10	5.15	3.18	21.95	.90	3.85	1.80
500	30.95	3.45	7.40	30.95	1.15	1.00	1.08	5.75	5.55	5.65	4.00	28.85	1.00	4.40	(2.35)
760	47.05	3.70	8.45	47.05	1.20	1.10	1.15	6.95	6.75	6.85	..	43.85	1.20	5.53	--

lyst at 0° are given in Figs. 2 and 3, respectively. The curves for measurements with the de-activated catalyst at 20° and at 0° before de-activation are similar in character.

With respect to the velocity measurements, it will be seen that the velocity (slope of curve) is greatest with a mixture of $2H_2$: $1C_2H_4$ (Curves I and IV) and least with a mixture of $1H_2$: $2C_2H_4$ (Curves III and VI). With a 50% mixture (Curves II and V) the velocity is intermediate between the other two. If the reaction were bimolecular, as the chemical equation suggests it might be, the velocity should be the same for the mixtures of $2H_2$:$1C_2H_4$ and $1H_2$:$2C_2H_4$, and with a 50% mixture the maximum velocity should be attained, that is, Curves I and III should coincide and Curve II should lie to their left. (The same holds for Curves IV and VI and Curve V.) The observed order of the curves suggests rather that the reaction is more nearly unimolecular with respect to hydrogen and independent of the ethylene concentration. As will be seen shortly, an excess of ethylene actually inhibits the reaction rather than causes an increase in velocity.

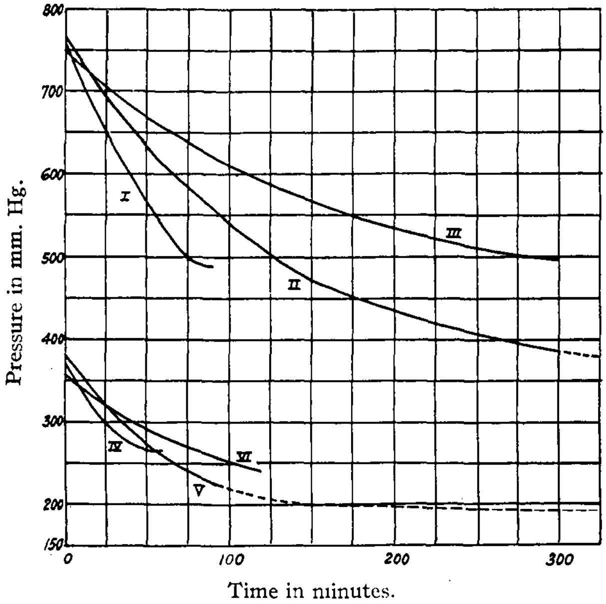

Fig 2.—Results of velocity measurements at 0° on partially de-activated catalyst. In I, II and III the initial pressure was 1 atmosphere; in IV, V and VI, 0.5 atmosphere.

Curve I—$2H_2$–$1C_2H_4$, Expt. 66; Curve II—$1H_2$–$1C_2H_4$, Expt. 62; Curve III—$1H_2$–$2C_2H_4$, Expt. 64; Curve IV—$2H_2$–$1C_2H_4$, Expt. 67; Curve V—$1H_2$–$1C_2H_4$, Expt. 63; Curve VI—$1H_2$–$2C_2H_4$, Expt. 65.

Effect of Hydrogen and Ethylene.—In order to get a measure of the effects of concentration of ethylene and hydrogen on reaction velocity, comparisons have been made of velocities, as measured by the decrease in pressure from the 5th to the 15th minute (ΔP), with the amounts of gas initially present in the bulb in two pairs of experiments in each of which the amount of one gas is approximately constant.

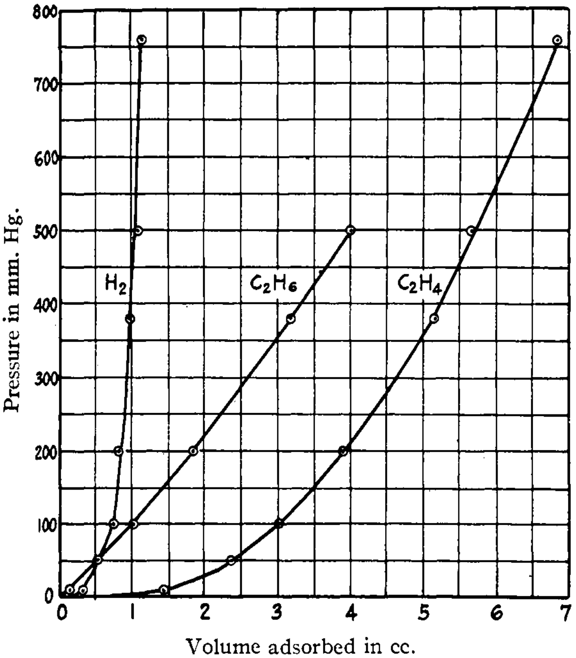

Fig. 3.—Adsorption of H_2, C_2H_4 and C_2H_6 at 0°. Curve for H_2—average of Experiments 57 and 71; Curve for C_2H_4—average of Experiments 58 and 70; Curve for C_2H_6—Experiment 56.

C_2H_4 Cc.	H_2 Cc.	ΔP Mm. Hg
17.25	8.65	14.5
16.95	33.80	43.0
Ratio	3.9	3.0

H_2 Cc.	C_2H_4 Cc.	ΔP Mm. Hg
17.15	8.60	30.5
17.30	34.55	18.0
Ratio	4.0	0.6

When the amount of ethylene is constant, increasing the hydrogen concentration 3.9 times causes the velocity to increase 3.0 times; and when the amount of hydrogen is kept constant, increasing the ethylene concentration 4 times causes the velocity to decrease to 0.6 of its original value; that is, with the same concentration of hydrogen, the reaction velocity *increases* 1.7 times when the ethylene concentration is *decreased* to $^1/_4$ of its original value.

It seems to the writer that a reasonable explanation of these observations can be made in terms of the adsorption theory of catalysis, with the aid of the results of the adsorption measurements. The adsorption of pure ethylene is markedly greater than that of pure hydrogen, being 1.45 cc. at 10 mm. pressure against 0.35 cc. for hydrogen, and 6.80 cc. at 760 mm. against 1.10 cc. for hydrogen. Since, therefore, the adsorption of ethylene at 10 mm. pressure is greater than that of hydrogen even at 760 mm., it is undoubtedly true that from almost any mixture of the two considerably more ethylene than hydrogen will be adsorbed. Further, if we suppose that those active centers on the catalyst surface which are capable of holding hydrogen are among those which can hold ethylene,[4] it follows that when there is a mixture of the two in contact with the surface they will be competing for these centers and, since the ethylene is the more strongly adsorbed, the hydrogen will occupy relatively few of such spaces. We shall, therefore, be dealing in most cases with a surface largely covered with ethylene, with hydrogen molecules scattered over it here and there. Let us suppose that both ethylene and hydrogen must be adsorbed before reaction can occur.[5] We have concluded that ethylene will usually be present in large excess on the surface, so that its surface concentration will be of secondary importance, so far as it enters directly into the velocity expression. The velocity should, therefore, depend mainly on the amount of hydrogen adsorbed. Other things being equal, the latter will increase with the partial pressure of the gas. It also seems reasonable to believe that as the partial pressure of ethylene, and therefore its adsorption, *decreases*, the amount of hydrogen adsorbed *at a given partial pressure* will *increase*. Since, therefore, we have assumed that the velocity depends upon the amount of hydrogen adsorbed, we may expect it to increase with increasing hydrogen concentration and decreasing ethylene concentration, within limits. These are the relationships found by experiment.

It has already been pointed out that with a constant quantity of ethylene (17.25 and 16.95 cc.) the reaction velocity triples when the hydrogen concentration is increased 3.9 times (from 8.65 cc. to 33.80 cc., Expts. 65 and 66). This may be taken to mean that the adsorption of hydrogen increases by a like amount under these conditions. Such a rate of increase in adsorption of hydrogen is markedly greater than the increase over the same concentration range in absence of ethylene. Under these conditions, 0.77 cc. of hydrogen is adsorbed from 8.65 cc. and 1.10 cc. from 33.80 cc. This would be an increase of only 1.7 times instead of 3 times. Our whole argument has been, however, that the presence of ethylene very markedly alters the adsorption of hydrogen as to amount, and there is no reason to believe the adsorption would not also be altered as to character. For

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[4] This is in harmony with the evidence already cited with respect to relation between partial pressures of ethylene and hydrogen and the initial pressure in a velocity experiment.

[5] Evidence for this is brought forward in a later section under "Experiments on a Catalyst Poisoned with Mercury."

the purposes of the analysis which follows, it has been assumed that the relation between hydrogen adsorbed and concentration in presence of ethylene could be calculated from that between reaction velocity and hydrogen concentration in Expts. 65 and 66 and that the relation is of the type $V_{\mathrm{H_2\,adsorbed}} = KV^n_{\mathrm{H_2\,total.}}$ The value so obtained for n is 0.8.

If those active centers on the catalyst surface which can hold hydrogen are also among those which can hold ethylene and if the ethylene is preferentially adsorbed, as has already been assumed, an increase in the amount of ethylene adsorbed will decrease the amount of surface available for holding hydrogen. We may assume that with sufficient ethylene all those centers which can hold hydrogen would be occupied by ethylene and no hydrogen would be adsorbed. We may represent the volume of ethylene which must be adsorbed to bring this about as a saturation capacity (which is not necessarily the saturation capacity of the surface for ethylene) and assume that the number of centers available for holding hydrogen is directly proportional to this saturation capacity less the amount of ethylene adsorbed. The latter will be assumed to be equal to the adsorption in the absence of hydrogen. Taking again reaction velocity as a measure of the amount of hydrogen adsorbed, the value for the saturation capacity has been calculated from the two experiments (64 and 67) in which the concentration of hydrogen was the same, that is, it has been assumed that in this case $\Delta P \doteq K$ (Sat. cap. $- V_{\mathrm{C_2H_4\,adsorbed}}$). The value so obtained for the saturation capacity is 9.30 cc. of ethylene adsorbed.

From the preceding considerations, there results the following expression for reaction velocity: $\Delta P = K_1.V_{\mathrm{H_2\,adsorbed}} = K_2.V_{\mathrm{H_2\,total}}(9.30 - V_{\mathrm{C_2H_4\,adsorbed}})$. The values of K_2 calculated from this equation are given in the following table.

Table III

The Reaction Velocity Constant at 0°

Initial volumes					
H_2 Cc.	C_2H_4 Cc.	C_2H_4 ads. Cc.	$9.30 - V_{\mathrm{C_2H_4\,ads.}}$	ΔP(5th – 15th min.) Mm. Hg	K_2
26.00	26.05	4.95	4.35	28.0	0.48
13.35	13.40	3.60	5.70	24.0	.53
17.30	34.55	5.55	3.75	18.0	.49
8.65	17.25	4.00	5.30	14.5	.49
33.80	16.95	4.00	5.30	43.0	.49
17.15	8.60	2.95	6.35	30.5	.50
26.00	26.00	4.95	4.35	31.0	.53
				Av.	.50

No special experiments were carried out to determine the effect of ethane on the reaction velocity, since it had been hoped that this could be obtained from a comparison of the results of velocity measurements at 0.5 and 1 atmosphere initial pressure. This has not appeared to be feasible for the reasons already stated in the introduction. Since ethane is not markedly adsorbed at low pressures as are hydrogen and ethylene, one would not expect it to be preferentially adsorbed in presence of these gases, from which it would follow that ethane would have little, if any, inhibitory effect. It is certainly true that there is no sign of a marked retardation toward the end of the experiments such as would result from serious interference by the product of the action, ethane.

Measurements at 20°.—Following the determinations at 0°, a series at 20° was carried out. During these experiments the catalyst bulb was immersed in water contained in a large Dewar vessel. The temperature was kept constant within 0.1° without difficulty by the addition from time to time of small quantities of water of suitable temperature.

Discussion of Results at 20°.—Values of the velocity constant have been calculated as in the case of the measurements at 0°. In order that the results should be strictly comparable with those at 0°, the values of ΔP should be reduced in the ratio 273:293. Since, however, there is also a correction of about the same magnitude to be applied because the ability of the surface to adsorb hydrogen is less at 20° than at 0° and since these two corrections act in opposite directions, neither has been made. The pressure decrease from the 5th to the 15th minute has been taken as before as a measure of reaction velocity. Since at 20°, this decrease is an appreciable fraction of the whole, there is less to be said in its favor. The value for the "saturation capacity" calculated at 0° has been used for 20° also. There are not sufficient data to check it at the higher temperature but it does not seem unreasonable to assume that since the surface is the same, the same value may be used.

The values calculated for K are given in the following table.

Table IV

$$\Delta P = K_1 V_{\text{H}_2\text{ ads.}} = K_2 V^{0.8}_{\text{H}_2\text{ tot.}}\ (9.30 - V_{\text{C}_2\text{H}_4\text{ ads.}})$$

H_2 total Cc.	C_2H_4 ads. Cc.	$9.30 - C_2H_4$ ads. Cc.	ΔP Mm. Hg	K_2
24.25	3.75	5.55	96.0	1.35
23.85	3.70	5.60	92.5	1.31
31.35	3.00	6.30	113.5	1.15
16.00	4.30	5.00	66.5	1.45
			Av.	1.32

It is worth noting that the constant is greatest when the amount of reaction is least, and *vice versa.* This is what one would expect as the result of taking for reaction velocity such large fractions of the total pressure decrease. The largest constant corresponding to the smallest rate is probably nearer the true value. In comparing the value of K with that at 0° we shall take the average value, however.

Temperature Coefficient.—The average value of the velocity constant is 0.50 at 0° and 1.32 at 20°. The velocity has therefore increased 2.64 times for a 20° rise in temperature. This is equivalent to an average temperature coefficient of 1.62 per 10° rise between 0° and 20°.

Such a great temperature coefficient effectually disposes of the possibility of diffusion playing a dominant part in the process. The increase in reaction velocity to be expected from diffusion alone would be about 2% per 10° instead of the 62% found. Moreover, if diffusion were a controlling factor, the velocity should depend upon the concentration of that reactant which would diffuse most slowly, namely ethylene, whereas actually it depends upon the concentration of the more rapidly diffusing hydrogen.

Experiments before De-activation of the Catalyst.—A short series of runs was made on the catalyst before de-activation by heating to 450°, in order that a comparison of the relative decreases in adsorption and catalytic activity might be made. The results of these experiments are given in Table I. A more complete series had already been carried out on another sample of catalyst. The velocity was so great, however, as to render the results somewhat untrustworthy. The behavior was in general like that with a less active catalyst.

It is not possible to put these results on the same basis as those obtained after de-activation because the adsorptions differ considerably. To get a rough idea of the relative velocities we may compare as before the pressure drop from the 5th to the 15th minute when the total amounts of gas present are about the same.

TABLE V

COMPARISON OF REACTION VELOCITY BEFORE AND AFTER DE-ACTIVATION

Before de-activation			After de-activation		
V_{H_2} Cc.	$V_{C_2H_4}$ Cc.	ΔP	V_{H_2} Cc.	$V_{C_2H_4}$ Cc.	ΔP
27.35	27.45	187	25.75	25.78	26
27.25	27.25	188	26.00	26.00	31
...	...	...	26.15	26.15	26.5
	Av.	188		Av.	28

De-activation thus caused the velocity to decrease to 15% of its original value. The adsorption at 0.5 atmosphere of hydrogen decreased to 30% (3.35 cc. : 1.00 cc.) and that of ethylene to 75% (6.85 cc. : 5.15 cc.) of their original values. At lower pressures the decreases in adsorption were somewhat greater. Thus, at 50 mm. that of hydrogen decreased to 24% of its original value (2.30 cc. : 0.55 cc.) and that of ethylene to 68% (3.55 cc. : 2.40 cc.). It is evident that the decrease in reaction velocity has followed more nearly the decrease in the ability of the surface to adsorb hydrogen.

Experiments on Catalyst Poisoned with Mercury.—Further information regarding the dependence of the reaction velocity upon the hydrogen adsorption was obtained in some experiments during which the catalyst was poisoned with mercury. No determinations of reaction velocity were made before poisoning but the magnitudes of the adsorptions indicate that the catalytic activity was somewhat greater than that of the catalyst already described. Several adsorption experiments were made and then a little mercury was run up into the stopcock of the manometer and blown into the evacuated catalyst bulb. The quantity of mercury was estimated from the bore of the stopcock to be 0.015 cc. or 200 mg. This would be equivalent to about 20 cc. of vapor at 0° and 760 mm. The bulb was then heated to 200° for $^1/_2$ hour and evacuated. After cooling, the mercury had disappeared and the catalyst was unchanged in appearance. The adsorptions at 380 mm. of hydrogen and ethylene, respectively, were found to be 3.25 cc. and 8.55 cc. before poisoning and 0.15 cc. and 6.70 cc. after poisoning. The value of ΔP for a 50% mixture after poisoning was 0.7 mm. and was estimated to be 200 mm. before poisoning.

It is evident that the mercury has reduced the adsorption of hydrogen to less than $^1/_{20}$ of its former value but has reduced the reaction velocity to about $^1/_{200}$ of its former value. The ethylene adsorption has been only moderately diminished. Here again it is evident that the catalyst must be able to adsorb hydrogen as well as ethylene before it can bring about reaction.

There is a marked similarity between the conclusions reached as a result of the investigation reported in this paper and those of Armstrong and Hilditch[6] from their experiments on the hydrogenation of unsaturated organic liquids in presence of metallic nickel. The essential reaction is the same in both cases, namely, the addition of hydrogen to a double bond. These authors have concluded that the hydrogenation proceeds by virtue of the formation of a complex involving the nickel catalyst, the unsaturated compound and hydrogen. They have found that when the hydrogen concentration is kept constant (by a flow method), the velocity is constant over 50 to 70% of the reaction, which is what one would expect in the case of the ethylene-hydrogen combination, if the same experimental conditions could be realized. They further found that when reaction did not give rise to catalyst poisons, the velocity increased in approximate proportion to the hydrogen concentration. So far as the writer knows, no experiments were carried out in the presence of an inert solvent to determine the effect of varying the concentration of unsaturated compound.

In the course of this investigation considerable data on the adsorption of gases by copper have been obtained which will be presented

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[6] Armstrong and Hilditch, *Proc. Roy. Soc.*, 1920–1922.

as such in a later paper. Among other things, it has been found that carbon monoxide is much more strongly adsorbed at low pressures than either ethylene or hydrogen and should consequently act as a catalyst poison in the ethylene-hydrogen combination. An investigation to demonstrate this has been begun. Work is also being started on the variation in the adsorption of ethylene and hydrogen with temperature. If reaction is contingent on adsorption, the apparent temperature coefficient of the reaction will evidently be composed of two factors, the normal increase in velocity with temperature and the decrease in surface concentrations of reactants for the same total concentrations, as the temperature is raised. Following the determinations of the temperature coefficients of adsorption it is planned to investigate further the temperature coefficient of the reaction. At temperatures in the vicinity of 200–300°, some work has already been done by Grassi,[2] who found that the coefficient was very small in this range. The writer has made a series of runs at 180–200° which bear this out. These will be published shortly.

Summary

1. The kinetics of the catalytic combination of hydrogen and ethylene in presence of metallic copper has been investigated at 0° and 20°; and measurements of reaction velocity and of adsorption isotherms have been made.

2. It has been found that within limits, the velocity increases with the hydrogen concentration but decreases as the ethylene concentration is increased, the particular relation being $\Delta P = K.V^{n}_{H_2\ \mathrm{tot.}}\ (V_{\mathrm{Sat.}} - V_{C_2H_4\ \mathrm{ads.}})$, in which ΔP is the pressure decrease from the 5th to the 15th minute; $V_{H_2\ \mathrm{tot.}}$ is the initial volume of hydrogen; $V_{\mathrm{sat.}}$ is the "Saturation capacity" of the surface for ethylene; $V_{C_2H_4\ \mathrm{ads.}}$ is the volume of ethylene adsorbed. For the catalyst most thoroughly investigated, $n = 0.8$ and $V_{\mathrm{sat.}} = 9.30$ cc.

The expression $V^{n}_{H_2\ \mathrm{tot.}}\ (V_{\mathrm{sat.}} - V_{C_2H_4\ \mathrm{ads.}})$ is taken to be proportional to the adsorption of hydrogen in presence of ethylene.

3. The temperature coefficient of reaction velocity has been found to be 1.62 per 10° rise, between 0° and 20°. It has been pointed out that this effectually disposes of the possibility of diffusion playing a dominant part in the process.

4. The similarity between the conclusions reached in this paper as to the kinetics of the ethylene-hydrogen combination and those of Armstrong and Hilditch as to the catalytic hydrogenation of unsaturated organic liquids has been pointed out.

The writer wishes to express his appreciation of the interest and advice of Professor Hugh S. Taylor of Princeton University in connection with this investigation.

This investigation was carried out with the aid of a National Research Fellowship in the Chemical Laboratory of Princeton University.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE INHIBITION OF THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN PEROXIDE SOLUTIONS. II

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Received February 21, 1923

In a preceding paper[1] an attempt was made to correlate the inhibitory action of a number of typical organic compounds with selective light absorption. The present investigation was instigated in order to study inhibition by some common inorganic acids, bases and salts, and to explain, if possible, the stabilizing action of organic compounds which obviously do not act by selective light absorption, and which include among their number two classes, the alcohols and amines.

With the exception of the nitrates,[2] which exhibit weak absorption throughout the ultraviolet, all the solutions studied were practically diactinic to the incident radiation; that is, all light absorption was due entirely to the hydrogen peroxide and not to the inhibitors.[3] Selective light absorption by inhibitors may be immediately ruled out as a cause.

The apparatus and experimental procedure were practically identical with those described in Part I[1] to which the reader is referred. There also will be found a complete definition of "inhibition constant" and a detailed account of experimental errors.

The materials used were the purest obtainable and were always tested for common impurities. The volatile acids were redistilled, and the salts were in a few cases recrystallized.

The inhibitory actions of the substances employed were compared by means of the inhibition constants. Bases were found to be excellent inhibitors, acids good, and neutral chlorides and bromides fair. No other inorganic compounds tried were found to inhibit. As was expected, inhibition was found to be independent of incident wave length. All measurements were made at a temperature of 25° unless otherwise stated. Many of the inhibitors have been previously studied by Henri and Wurm-

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[1] Anderson and Taylor, THIS JOURNAL, **45**, 650 (1923).

[2] Winther, Baggesgaard-Rasmussen and Schreiner, *Z. wiss. Phot.*, **22**, 33 (1922). Hartley, *J. Chem. Soc.*, **83**, 221 (1903); **81**, 571 (1902).

[3] Miller, *Phil. Trans.*, **152**, 861 (1863). Martens, *Drude's Ann.*, **6**, 603 (1901). Houston, *Proc. Roy. Soc. Edinburgh*, **32**, 40 (1912). Retschinsky, *Ann. Physik*, **42**, 1580 (1913). Brannigan and Macbeth, *J. Chem. Soc.*, **109**, 1277 (1916). Wright, *ibid.*, **103**, 528 (1913). Henri and Wurmser, *Compt. rend.*, **156**, 1012 (1913).