Summary

1. The photochemical decomposition of ammonia by relatively short wave lengths has been studied. It is found that for the approximate region of the spectrum between 190 and 160mμ, 1.4 quanta are absorbed per molecule decomposed. This is based on the assumption that two molecules of ozone are produced from oxygen per quantum absorbed. The quantum efficiency is higher in this region of the spectrum than that found by other authors in the neighborhood of 210mμ.

2. A short theoretical discussion is given. It does not seem possible to give a mechanism for the reaction which is free from all criticism, but with the use of thermal data it is possible to indicate which reactions might be possible. The increase in quantum efficiency with increase in frequency of radiation receives a reasonable qualitative explanation on the basis of recent theories of band spectra.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 38]

THE CATALYTIC COMBINATION OF ETHYLENE AND HYDROGEN IN THE PRESENCE OF METALLIC COPPER IV. KINETICS AT 100 AND 220°, THE TEMPERATURE COEFFICIENT BETWEEN 0 AND 220°, AND SUMMARY

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Previous work[1] on the hydrogenation of ethylene in the presence of copper has shown that at 0° the rate is increased by excess of hydrogen but decreased by excess of ethylene, while at 200° the rate indicates an approximation to a bimolecular reaction, in which case proportionate increases in rate are caused by excess of either hydrogen or ethylene. Obviously, at some intermediate temperature the reaction rate should be independent of the ethylene concentration and proportional to the hydrogen concentration alone. We have thought it worth while to investigate this case and at the same time to obtain additional data on the higher temperatures. Further, we have taken occasion to measure rates at a series of temperatures between 0 and 200° in order to obtain the conventional heat of activation of this reaction.

The apparatus and general method of procedure have been fully described in previous papers.[1b] Suitable gas mixtures were made up in a calibrated gas buret and run into the evacuated catalyst chamber. The rate of reaction was then followed by the pressure decrease at constant volume.

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[1] (a) Grassi, *Nuovo Cimento*, [6] **11**, 147 (1916); (b) Pease, THIS JOURNAL, **45**, 1198, 2235 (1923).

Two catalysts were used, one of which was partially deactivated by heating in order to carry out the measurements at intermediate temperatures. One of these catalysts consisted of approximately 10% by weight of copper on broken diatomite brick (kindly furnished by the Armstrong Cork Co.). The brick was sized to 4–10 mesh, thoroughly washed with nitric acid, dried and impregnated uniformly with the proper amount of copper nitrate solution. This solution was made up to such a concentration that its weight was approximately that of the brick, since the latter will take up its own weight of water without becoming distinctly wet. After slow drying, the catalyst was reduced in hydrogen at 200°. Sixty cc. of catalyst was used. The second catalyst was prepared by coating glass beads with metallic copper, precipitated from a warm alkaline solution of cuprous hydroxide with phenylhydrazine. The method is due to Chattaway,[2] and gives a uniform bright copper coating; 575 glass beads of average diameter 0.486 cm., possessing a total surface of 426 sq. cm., carried 0.409 g. of copper. The purpose of this type of catalyst was to get away from possible solution effects.

The brick-supported catalyst used in the present work did not prove as active as the bulk catalyst used earlier,[3] and a comprehensive series of measurements at 0° was not attempted. The first such measurements were at 50°. As the disturbing effect of ethylene still persisted, the catalyst was partially deactivated by heating to 500° for eight hours in a vacuum. This treatment gave a catalyst of moderate activity at 100°.

Experiments at 100°.—The results of thirteen experiments at 100° are summarized in Table I. The initial rates were obtained by extra-

TABLE I

KINETICS AT 100°C.

Expt. No.	Ratio, $H_2:C_2H_4$	Partial press., atm. H_2	C_2H_4	dp/dt mm./min.	$\frac{dp}{dt}\cdot\frac{1}{pH_2}$ $\frac{\text{mm.}}{\text{min.}}\cdot\frac{1}{\text{atm.}}$
141	2:1	$1/3$	$1/6$	21.5	65
142	3:1	$3/8$	$1/8$	23.5	62
143	1:2	$1/6$	$1/3$	12.5	74
146	1:1	$1/2$	$1/2$	33.3	67
147	1:2	$1/3$	$2/3$	21.0	63
148	2:1	$2/3$	$1/3$	43.0	65
149	3:1	$3/4$	$1/4$	42.2	56
150	1:3	$1/4$	$3/4$	16.0	64
151	1:1	$1/4$	$1/4$	16.2	65
152	2:1	$1/3$	$1/6$	21.4	64
153	1:2	$1/6$	$1/3$	10.9	64
154	3:1	$3/8$	$1/8$	24.0	65
155	1:3	$1/8$	$3/8$	8.5	65

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[2] Chattaway, *Chem. News*, **96**, 85 (1907).

[3] This is due, perhaps, to a smaller surface area.

polation, and are compared with the initial partial pressures. The latter are calculated from the composition of the mixture and the initial pressure. The adsorptions of ethylene and hydrogen on this catalyst were not determined at 100°. At 50°, before deactivation, 0.15 cc. of hydrogen and 3.10 cc. of ethylene were adsorbed at 1 atm. and 0.15 cc. of hydrogen and 2.35 cc. of ethylene at $^1/_2$ atm. It is to be presumed that the deactivated catalyst would have adsorbed a negligible amount of hydrogen and something less than 1 cc. of ethylene at 100° and 1 atm. If adsorption were taken into account, the partial pressure of hydrogen would be increased and that of ethylene decreased slightly.

It is clear that over the range investigated the reaction rate is proportional to the hydrogen concentration alone, and the reaction is, therefore, monomolecular with respect to hydrogen and of zero order with respect to ethylene. This represents the transition from the behavior at low temperatures, when ethylene inhibits the reaction, to higher temperatures, when the reaction rate increases in proportion to the ethylene partial pressure.

Experiments at 220°.—In the original work at higher temperatures, the bulk copper catalyst was found to adsorb hydrogen very slowly. As it was thought that this might have interfered somewhat with the pressure measurements, new experiments have been carried out using as catalyst a film of copper deposited on glass beads. It was found that individual experiments gave very good bimolecular constants. Excess of ethylene, however, leads to an appreciably lower constant, as was found in the earlier work. Thus, the reaction is nearly but not quite normally bimolecular even at 220°. The average values of $K = (\mathrm{d}p/\mathrm{d}t)(1/p\mathrm{H}_2.p\mathrm{C}_2\mathrm{H}_4)$ are given below; p is in millimeters of mercury, t is in minutes.

TABLE II

AVERAGE BIMOLECULAR CONSTANTS AT 220°

Initial mixture atm. H_2	atm. C_2H_4	$K \times 10^4$
$^1/_2$	$^1/_2$	1.8
$^2/_3$	$^1/_3$	2.0
$^1/_3$	$^2/_3$	1.75
$^1/_2$	$^1/_2$	1.9

The results are much the same as those previously obtained. The catalyst is about as active as a bulk copper catalyst deactivated at 500°.

Temperature Coefficient.—Runs were carried out with a 50% mixture, initially at 1 atmosphere, between 0 and 220°. From 0 to 60° the brick-supported catalyst before heat treatment was used; from 60 to 100° the brick-supported catalyst after heat treatment; from 194 to 220° the catalyst consisted of copper deposited on glass beads.

The question arises as to the basis upon which to compare rates at different temperatures, since the reaction kinetics change as the temperature rises. A complete expression for the latter would take account of this. Full data on the rate at each temperature and on the small adsorptions would be required, however, and we have not thought it worth while to obtain these. Instead, we compare rates at equal pressures ($^1/_2$ atmosphere of each gas) and obtain therefrom the conventional heat of activation. The difference between this and the true heat of activation involves terms for the heats of adsorption.

The reaction velocity curves have been extrapolated back to 1 atmosphere initial pressure and the tangent taken at this point. The latter are taken as the velocity constants at each temperature. They are given in Table III along with values of A, the conventional heat of activation calculated from $\log \frac{k_2}{k_1} = \frac{A}{4.58}\left(\frac{T_2 - T_1}{T_1T_2}\right)$.

TABLE III

HEATS OF ACTIVATION

Temp., °C.	dp/dt (1 atm.) = "k" (mm. per min.)	A, cal.
Brick-supported catalyst before deactivation		
0	0.358	
		13,350
10	0.853	
		16,500
20	2.32	
		12,150
30	4.62	
		13,000
40	9.21	
		11,450
50	16.27	
		13,800
60	31.0	
	Av.	13,400
Brick-supported catalyst after deactivation		
60	4.06	
		14,050
78.5	12.4	
		12,300
100	34.1	
	Av.	13,200
Copper film on glass beads		
194	14.6	6000
220	20.5	

It is clear that the conventional expression for temperature coefficient applies from 0 to 100°, and that deactivation of the brick-supported catalyst does not change the heat of activation. The lower value in the

194–220° range is characteristic of the reaction, not of the unusual catalyst. The data of Grassi[1a] and of Pease[1b] lead to the same result. Thus, Pease calculated the heat of activation to be 7000 cal. between 200 and 250°. Between 150 and 200° it was 10,800 cal. These values were obtained on the same sample of bulk copper catalyst in the same state of activation. Grassi's data give 12,000 cal. between 150 and 200°, and only 1300 cal. between 200 and 250°. Between 250 and 275° he found the temperature coefficient to be zero. A similar decrease in temperature coefficient is noticeable in the results of Morris and Reyerson on the hydrogenation of ethylene in presence of copper, platinum and palladium deposited on silica gel.[4]

Theoretical Interpretation.—In concluding for the present this work on the hydrogenation of ethylene in the presence of copper, it may be of interest to summarize it briefly and supply the interpretation based on Langmuir's theory of adsorption and surface catalysis.[5]

The Langmuir theory assumes that reaction takes place on the catalyst surface in a layer of adsorbed gas not more than one molecule deep. The reaction kinetics, therefore, depend on the adsorptions as these are affected by pressure and temperature changes.

Assuming, with Langmuir, the monomolecular film, assuming that every molecule striking bare surface condenses and that the amount adsorbed depends chiefly on the rate of evaporation, one obtains for the fraction, x, of surface covered: $x = k_1p/(k_2 + k_1p)$, where p is the pressure, k_1 is the rate of condensation on a free surface (and is practically equal to the number of impacts) and k_2 is the rate of evaporation from the completely covered surface. With small adsorptions, x is proportional to the pressure; with a nearly covered surface, x slowly approaches unity, and the fraction $(1 - x)$ of surface free of gas varies inversely as the pressure $(1 - x)p = k_2/k_1$. The adsorption changes with temperature on account of the variation of k_2, the unit rate of evaporation, chiefly. The function is doubtless of the "vapor pressure" type, so that $d \ln k_2/dt = Q/RT^2$, where Q is approximately the heat of adsorption.

Assuming k_1 independent of temperature (the square root of temperature is involved), this results, in the case that the adsorption is small ($x = k_1p/k_2$), in x decreasing with the temperature in the same way that k_2 increases, pressure being constant. When the adsorption is large, so that —$(1 - x)p = k_2/k_1$, the fraction $(1 - x)$ of surface bare of gas increases with the temperature in the same way as k_2 increases, pressure being constant.

The above are the relations which we shall apply to the ethylene-hydrogen reaction. It is to be remembered that the fundamental equation

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[4] Morris and Reyerson, *J. Phys. Chem.*, **31**, 1224 (1927).

[5] Langmuir, THIS JOURNAL, **38**, 2221 (1916).

expresses a limiting law. In particular, it assumes a uniform surface. Poisoning experiments with carbon monoxide,[6] and other data indicate that this condition is very far from applying. Nevertheless, the "active" surface may be considered to be meant in this case.

We consider first the low temperature experiments. At 0° both ethylene and hydrogen are strongly adsorbed, the ethylene adsorption being the higher of the two. Ethane is loosely adsorbed only. The rate is approximately proportional to the hydrogen concentration and inversely as a fractional power of the ethylene concentration. We suppose that molecules of the two gases must be in favorable juxtaposition on the catalyst surface for reaction to occur, and that in view of the stronger adsorption of ethylene, the surface is largely covered with this gas. Then the fraction $(1 - x)$ of surface free of ethylene, and available for condensation of hydrogen, would be inversely proportional to the ethylene partial pressure. At a given partial pressure of ethylene, the chance that a hydrogen molecule will strike a vacant spot on the surface is proportional to its pressure. The resulting reaction would then take place at a rate proportional to the hydrogen pressure and inversely proportional to the ethylene partial pressure. The experimental results approximate to this sufficiently closely to warrant the conclusion that this expresses fairly accurately the actual condition. If reaction followed immediately on condensation of hydrogen on a vacant spot, the above relations should hold somewhat better. Actually there is probably some lag, so that at any moment there are both hydrogen and ethylene molecules on the surface, the effect being to complicate somewhat the relations of adsorptions to pressures.

In the simple case, the effect of temperature would be to increase the fraction $(1 - x)$ of surface free of ethylene, and to increase the rate in proportion to $(1 - x)$. The temperature coefficient of reaction would then be equal to that of k_2, the unit rate of evaporation of ethylene from the surface. This assumes that the temperature coefficient of the surface reaction is zero, which is probably not the case. Actually the temperature coefficient probably includes as well a term for the surface reaction. In either case the rate should increase exponentially with temperature, as is found between 0 and 100°.

The preceding discussion covers one limiting case. At the other extreme, namely, at high temperatures with a very inactive catalyst and small adsorptions, there is to be expected a bimolecular reaction with a negative temperature coefficient. This follows from the conclusion that with small adsorptions the amount adsorbed (fraction of surface covered) will be proportional to the pressure ($x = k_1p/k_2$). The chance that molecules of ethylene and hydrogen will be favorably situated for

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[6] Pease and Stewart, This Journal, **47**, 1235 (1925).

reaction is then proportional to the product of the pressures. With varying temperature and constant pressure, x will vary inversely as k_2 (the unit rate of evaporation) for each gas. Since k_2 increases with the temperature, x will decrease. At the highest temperatures, the surface reaction rate will become infinite, so that every time molecules of the two gases are suitably disposed on the catalyst surface, reaction will occur. The temperature coefficient of reaction will then be the product of the temperature coefficients of the unit rates of evaporation, and will be negative.

It was found that at 200 and 220° the reaction is in fact nearly bimolecular, and the temperature coefficient undoubtedly will be negative at about 300° and higher. At 250° it is practically zero. At 200° ethylene is still somewhat inhibiting the reaction, however, and this, together with a probable increase in the surface reaction rate with temperature in this range, accounts for the temperature coefficients being still positive.

The conditions at 100° correspond to a transition from low temperatures and large adsorptions, when ethylene inhibits, to high temperatures and small adsorptions, when ethylene behaves normally. Large ethylene adsorptions interfere with reaction by preventing condensation of hydrogen. Smaller ethylene adsorptions allow more hydrogen molecules to condense, but increase the possibility of a condensing hydrogen molecule finding no ethylene in proximity with which to react. The two effects seem to neutralize each other at 100° over the pressure range studied.

The characteristics of the ethylene-hydrogen reaction in the presence of copper closely duplicate those of the hydrogen-oxygen reaction in the presence of platinum, which has been thoroughly investigated by Langmuir.[7] In the latter hydrogen inhibits the reaction at low temperatures and the temperature coefficient is positive. Stoichiometric relations and a negative temperature coefficient are observed at high temperatures. The kinetics are, therefore, much the same in the two cases.

Summary

1. It has been found that at 100° the hydrogenation of ethylene in the presence of copper takes place at a rate proportional to the hydrogen concentration and independent of the ethylene concentration over partial-pressure ranges of $^1/_8$ to $^3/_4$ atmospheres.

2. It has been shown that at 220° the reaction is nearly but not quite bimolecular.

3. Rates have been measured between 0 and 220° and heats of activation calculated. The normal expression has been shown to apply between 0 and 100°. At higher temperatures there is a marked decrease in temperature coefficient and in heat activation.

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[7] Langmuir, *Trans. Faraday Soc.*, **17**, 621 (1922).

4. The results of these and earlier experiments on this reaction are summarized and interpreted.

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NOTE

Note on a Light Source for Continuous Spectrum.—Since the introduction of the photometric methods for the determination of the quantitative absorption of light by solutions, much difficulty has been experienced in finding a suitable light source. A Tesla spark under water fulfils most nearly the requirements but previous designs[1] of such lamps have not been satisfactory for general or continuous use.

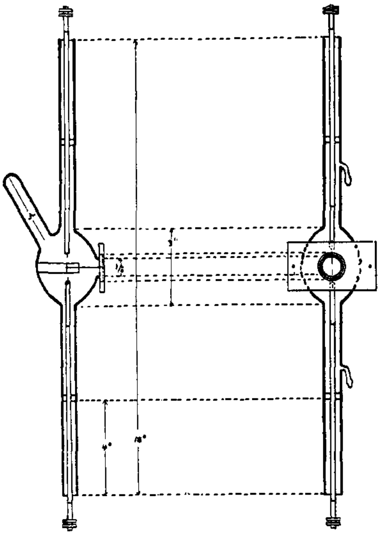

Fig. 1.—Continuous spectrum light source.

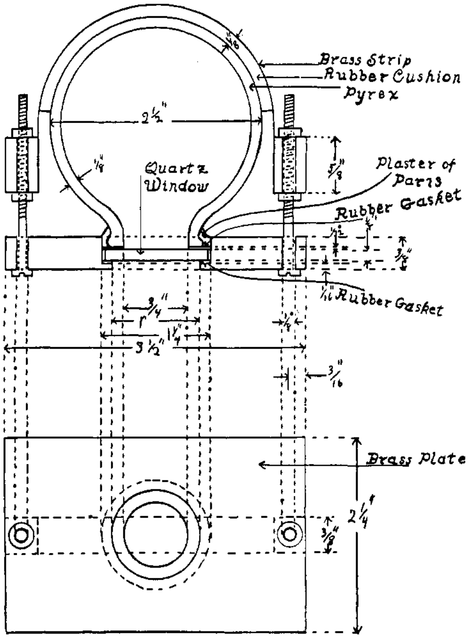

Fig. 2.—Continuous spectrum light source, detail of window clamp.

The accompanying cuts show the details of the completed lamp. Some points about its construction ought, however, to be mentioned. The glass sleeves carrying the brass rods are fire-polished until the inside diameter is slightly less than the diameter of the brass rod. The split end of the brass rod is then compressed and used to grind one end of the glass sleeve until the rod passes through to the other end where the grinding is continued. The two ground ends hold the brass rod rigidly in position.

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[1] The most recent of these is described in the Bureau of Standards Scientific Papers, No. 440.