Beer's law over a range in concentration suitable for colorimetric analysis. The sensitivity, optimum experimental conditions and the effect of various ions have been determined. Best results were obtained with a 0.05% reagent solution and a nickel concentration of ten mg. per liter. The reagent will detect one part of nickel in 125 million parts of solution, when the observation is made in a 50-ml. (210-mm.) Nessler tube. The color develops satisfactorily in sulfuric acid solution up to approximately 0.002 normal. Traces of alkali cause fading. Many metallic ions give color reactions with the reagent and hence will interfere with the nickel determination unless they are removed. Iron and cobalt are the ions most likely to interfere and must be removed unless the nickel concentration is at least a hundred times greater than that of these ions.

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THE HOMOGENEOUS COMBINATION OF ETHYLENE AND HYDROGEN. A SECOND-ORDER ASSOCIATION REACTION

BY ROBERT N. PEASE

It has recently been shown that the polymerization of ethylene at pressures above one atmosphere is a second-order homogeneous gas reaction.[1] The primary action is thus of the association type. In view of the fact that many homogeneous dissociation reactions are known to be first order, it was inevitable that second-order homogeneous association reactions should occur, unless the classical principle of mobile equilibrium is incorrect as ordinarily applied. Nevertheless, a theoretical difficulty has arisen in this connection which makes it especially desirable to investigate other cases. The hydrogenation of ethylene is a particularly suitable example since the reaction is reversible,[2] and the reverse action (dissociation of ethane) has been rather definitely shown to be first order.[3]

The theoretical difficulty mentioned above has to do with the accommodation of energy in a single product molecule newly formed by the collision of two reactant molecules. A rather crude analogy on a large scale is the cohesion of two "sticky" masses—say, two balls of tar—which have been directed at each other. In the latter case, any kinetic energy which is lost, and the cohesion energy are converted into internal energy of the resulting mass. Similarly in the case of two associating molecules, the

[1] Pease, THIS JOURNAL, **53**, 613 (1931). At lower pressures there is evidence of deviation. See Pease, *ibid.*, **52**, 1158 (1930). The polymerization of acetylene may also be second order. See Pease, *ibid.*, 51, 3470 (1929).

[2] Pease and Durgan, *ibid.*, **50**, 2715 (1928).

[3] Marek and McCluer, *Ind. Eng. Chem.*, **23**, 878 (1931); Frey and Smith, *ibid.*, **20**, 948 (1928).

product molecule is called upon to accommodate in internal degrees of freedom any loss of kinetic energy due to the inelastic nature of the collision, plus the reaction energy, and the internal energies of the original molecules. However, since internal degrees of freedom are in general quantized, the chance that the product molecule should be able to do this appears to be negligible. The association is, therefore, extremely improbable.

The solution of this apparent difficulty was suggested by Kassel.[4] The above argument implies that the internal degrees of freedom must be quantized *immediately* the molecule is formed. This cannot be assumed. Rather, the uncertainty principle indicates that the energies of individual states may differ from their final values by as much as $h/\Delta t$, where Δt is the time from the instant of collision. Therefore, if the total energy levels are spaced sufficiently closely, any value of the energy may be temporarily accommodated by the product molecule. Eventually, of course, any excess of energy over that exactly corresponding to some particular set of energy levels must be converted into kinetic energy in another collision, if the product molecule is to be stabilized.

The simplest reaction mechanism appears to be essentially that suggested by Taylor for the ethylene polymerization.[5] Two molecules whose joint energy exceeds some minimum may unite on collision. The resulting quasimolecule may subsequently either dissociate spontaneously, or it may be dissociated as a result of a collision, or, finally, it may be stabilized as a result of a collision. Which of the last two happens will depend on the state of the molecule at the instant of collision. The rate of association will be

$$\alpha Z_0 e^{-E/RT} c_1 c_2$$

where α is an orientation factor, Z is the total collision rate at unit concentrations and E is the activation energy. If most quasi-molecules of products survive to undergo a collision (instead of decomposing spontaneously), the observed reaction rate will then be given by

$$\alpha \beta z_0 e^{-E/RT} c_1 c_2$$

where β is the fraction of subsequent collisions in which the quasi-molecule is stabilized, rather than decomposed. In the case of ethylene polymerization the product $\alpha\beta$ was found to be about $1/2000$. As will be shown later, it is more nearly unity for the hydrogenation of ethylene.

Apparatus and Method

The apparatus and method were standard. The reaction was followed by measuring the pressure decrease at constant volume in a heated Pyrex reaction vessel of 500 cc. volume. After a measurement was completed, the reaction mixture was collected with a Töpler pump and analyzed.

[4] Kassel, THIS JOURNAL, **53**, 2143 (1931).

[5] Pease, *ibid.*, **53**, 613 (1931).

The hydrogen was purified by passage over hot platinized asbestos, and through a trap at $-79°$. The ethylene was purified by fractionation. Both gases were originally better than 99% pure.

Results

The experiments were subject to two limitations. Owing to simultaneous polymerization of ethylene, it was necessary to confine the measurements to mixtures containing a 3:1 excess of hydrogen. Satisfactory results were then obtained when the reaction vessel was unpacked. When, however, the vessel was filled with broken glass, it was found that considerable quantities of hydrogen were absorbed by the latter.[6] As a result, the observed pressure decrease (at 550°) was about twice that with the empty vessel. Analysis of the gas reaction mixture after exposure showed clearly that the rate of ethane formation was normal. This is the more interesting since it shows that the absorbed hydrogen is not reactive.

The values of k_2 were calculated by means of the equation

$$k_2 = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

where t is the time in seconds, a is the initial pressure of hydrogen, b is the initial pressure of ethylene and x is the pressure of ethane at time t. In calculating values of k_2, the first measurement ($t = 300$) was taken as the initial state.

Since the reaction is reversible, it was necessary to determine whether the reverse action was interfering to an appreciable extent. It was found that the values of k_2 were not appreciably different when the much more elaborate expression involving the rate of the reverse action was employed. Measurements were only carried up to 50% conversion of the ethylene.

The results of a series of experiments with $3H_2:1C_2H_4$ mixtures carried out in the unpacked reaction vessel are presented in Table I. It will be seen that the values of k_2 are reasonably constant at each temperature. At 550° measurements were made with initial total pressures of one, one-half and one-fourth atmosphere. Although the constants at one-half atmosphere were somewhat lower than the others, there is no reason to doubt that the reaction is second-order.

It has already been mentioned that polymerization of ethylene interfered when the reaction mixture contained more than 25% of this gas. This is shown by the data of Table II. Two runs were made at 550° with mixtures of $2H_2:1C_2H_4$ and $1H_2:1C_2H_4$. In each case the amount of hydrogen reacting was nearly the same as the amount of ethane formed. The amount of ethylene reacting exceeded this latter by 11% with the $2H_2$:-$1C_2H_4$ mixture, and by 33% in the $1H_2:1C_2H_4$ mixture. In consequence it is not possible to calculate a constant for the formation of ethane. Ap-

[6] Compare Alyea, This Journal, 53, 1324 (1931).

TABLE I

RATES WITH 3H₂:1C₂H₄ MIXTURES IN EMPTY REACTION TUBE

Temp., °C.	475		500		524		552		548		550	
Initial press. H₂, mm.	573		575		580		562		294		141	
Initial press. C₂H₄, mm.	195		196		198		191		100		48	
Initial total press., mm.	768		771		778		753		394		189	

Time, sec.	Obs. press.	$k_2 \times 10^7$	Obs. press.	$k_2 \times 10^7$	Obs. press.	$k_2 \times 10^7$	Obs. press.	$k_2 \times 10^7$	Obs. press.	$k_2 \times 10^7$	Obs. press.	$k_2 \times 10^7$
300	762		756		747		717		380		183	
600	758	(1.3)	749	2.43	733	5.39	685	15.1	371	13.4	180	(19)
900	755	(1.1)	743	2.25	720	5.50	661	15.1	363	13.6	178	16
1200	752	1.08	737	2.24	709	5.42	Av.	15.1	356	13.6	176	15
1800	747	0.99	725	2.31	690	5.37			345	13.4	172	16
2700	739	0.98	708	2.40	667	5.40			Av.	13.5	168	15
3600	732	0.95	693	2.47	Av.	5.42					Av.	16
4500	723	1.01	680	2.51								
7200	703	1.01	Av.	2.37								
	Av.	1.00										

Final press. change, mm.	65	91	111	92	49	21
C₂H₆ formed, mm.	64	92	119	108	58	28
C₂H₄ used, mm.	60	87	107	89	47	24
H₂ used, mm.	69	96	124	112	62	25

TABLE II

REACTION AT 550° WITH 2H₂:1C₂H₄ AND 1H₂:1C₂H₄ MIXTURES

Temp., °C.	548	550
Initial % C₂H₄	33.1	49.2
Initial total press., mm.	768	766
Final total press., mm.	620	565
Pressure drop, mm.	148	201
C₂H₆ formed, mm.	141	184
H₂ reacted, mm.	146	187
C₂H₄ reacted, mm.	157	245
CH₄ formed, mm.	10	35
Higher unsats. formed, mm.	4	12
Reaction time, sec.	1800	2700
$k_2 \times 10^7$	(11.4)	(10.7)

proximate calculations indicate that the value of k_2 may be somewhat less in these mixtures. Thus, the most favorable view that could be taken would be that the whole pressure drop is due to ethane formation. The corresponding calculation of k_2 gives 11.4×10^{-7} for the 2H₂:1C₂H₄ mixture, and 10.7×10^{-7} for the 1H₂:1C₂H₄ mixture, as compared with 15.1×10^{-7} for the 3H₂:1C₂H₄ mixture.

Experiments with the reaction vessel filled with broken Pyrex glass (4–10 mesh) are recorded in Table III. Analysis showed that in all cases there was a marked loss of hydrogen in excess of ethane formed. In this case also it is not possible to give precise values of k_2. Assuming that the whole pressure drop represents reaction, the values of k_2 would be 4.15×10^{-7} at 500° and 1 atm. (initial), and 27.4×10^{-7} at 550° and 1 atm. (initial). These are to be compared with 2.37×10^{-7}, and 15.1×10^{-7}, respectively,

in the empty tube. The constants for the packed tube are nearly twice those for the empty tube. Even if this were all due to increased wall reaction in the packed tube, it would still not be serious since the wall surface has been increased by a factor of ten at least. However, the results of analysis show clearly that twice as much hydrogen as ethylene has disappeared, which accounts for the large apparent value of k_2. In the experiment at 550° the final reaction mixture was fractionated before analysis. The result proved that ethane, rather than a mixture of methane and propane (say), was produced.

TABLE III

REACTION OF $3H_2:1C_2H_4$ MIXTURE IN PACKED REACTION VESSEL

Temp., °C.	499	550	550
Initial press. H_2, mm.	564	563	335
Initial press. C_2H_4, mm.	193	193	115
Initial total press., mm.	757	756	450
Final total press., mm.	694	648	390
Pressure drop, mm.	63	108	60
C_2H_6 formed, mm.	45	83	39
H_2 reacted, mm.	72	126	68
C_2H_4 reacted, mm.	38	65	31
Reaction time, sec.	1800	600	900
$k \times 10^7$	(4.15)	(27.4)	(27.3)

Discussion

The results show that the formation of ethane from ethylene and hydrogen is a homogeneous, second-order reaction, at least when hydrogen is in excess. It remains to calculate the reaction rate on the basis of the collision theory.

The values of k_2 for the runs at one atmosphere in the empty bulb with a $3H_2:1C_2H_4$ mixture are fitted by the equation

$$\log_{10} k_2 = -\frac{43{,}150}{2.303RT} + 5.576$$

as shown by the data of Table IV.

TABLE IV

COMPARISON OF CALCULATED AND OBSERVED VALUES OF k_2

Temp., Å.	Obs.	Calcd.
	$k_2 \times 10^7$	
748	1.00	0.97
773	2.37	2.45
797	5.42	5.70
825	15.1	14.5

According to the collision theory, the rate of reaction in terms of molecules of ethane formed per cc. per second should be

$$\alpha\beta 2\sqrt{\frac{2\pi RT(M_1 + M_2)}{M_1 M_2}}\ \sigma_{12}^2 n_1 n_2 e^{-43{,}150/RT}$$

where M_1 is the molecular weight of H_2, M_2 is the molecular weight of C_2H_4, σ_{12} is the average diameter of H_2 and C_2H_4 in cm., n_1 is the number of mols. of H_2 per cc. and n_2 is the number of mols. of C_2H_4 per cc. α and β have been already defined. Since σ_{12} can only be approximately estimated in the absence of viscosity determinations at the temperatures of the experiments, it seems best to use the velocity data to calculate $\alpha\beta\sigma_{12}^2$. An estimate of $\alpha\beta$ can then be made by substituting a reasonable value of σ_{12}.

k_2 represents the pressure in mm. of C_2H_6 formed per second when C_2H_4 and H_2 are at 1 mm. pressure each. At 500° (773 Å.) k_2 is 2.45×10^{-7}. This corresponds to 3.08×10^9 molecules of C_2H_6 formed per cc. per second. At 550° and 1 mm. pressure there will be 1.25×10^{16} molecules each of H_2 and C_2H_4 per cc. Substituting

$$\frac{3.08 \times 10^9}{(1.257 \times 10^{16})^2} = \alpha\beta\sigma_{12}^2 . 2\sqrt{\frac{2\pi 8.32 \times 10^7 \times 773 \times 28.0}{24.0 \times 4.03}} . e^{-\frac{43,150}{1.985 \times 773}}.$$

$$\alpha\beta\sigma_{12}^2 = 4.38 \times 10^{-17}$$

If now we assume that

$$\sigma_{H_2} = 1 \times 10^{-8}$$
$$\sigma_{C_2H_4} = 4 \times 10^{-8}$$

then

$$\sigma_{12}^2 = 4 \times 10^{-16}$$

whence $\alpha\beta = 0.1$, approximately. Thus, of all collisions between H_2 and C_2H_4 molecules having the requisite energy, about 10% lead to formation of C_2H_6. This is to be compared with 0.05% (1/2000) in the combination of ethylene molecules.

Comparison with Equilibrium Data and Rate of Dissociation of Ethane.—If the velocity constant for the combination of ethylene and hydrogen is k_2, and the constant for dissociation of ethane is k_1, the equilibrium constant for the dissociation of ethane

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

is given by

$$K = \frac{p_{C_2H_4}p_{H_2}}{p_{C_2H_6}} = \frac{k_1}{k_2}$$

The experiments here reported give for k_2 in mm.

$$\log_{10}k_2 = -\frac{43,150}{2.3RT} + 5.576$$

For k_2 in atmospheres, this becomes

$$\log_{10}k_2 = -\frac{43,150}{2.3RT} + 8.457$$

For k_1, the work of Marek and McCluer[3] gives

$$\log_{10}k_1 = -\frac{73,170}{2.3RT} + 15.12$$

Thus

$$\log_{10}K = \log_{10}k_1 - \log_{10}k_2 = -\frac{30,020}{2.3RT} + 6.66$$

Direct measurements of K at 600–700° give[2]

$$\log_{10} K = -\frac{31{,}244}{2.3RT} + 6.31$$

The independent determinations thus confirm one another.

Summary

The combination of ethylene and hydrogen in a Pyrex glass vessel at 475–550° and one atmosphere pressure has been shown to be a homogeneous, second-order reaction. A calculation based on the collision theory indicates that about 10% of the collisions between ethylene and hydrogen molecules possessing the requisite energy (43,150 cal. per mole) eventually result in formation of ethane.

Combination of equations for the rates of ethane formation and of ethane dissociation gives an equation for the equilibrium constant of the reaction

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

in good agreement with that obtained by direct measurement.

PRINCETON, NEW JERSEY

THE PREPARATION AND PROPERTIES OF IODINE MONOCHLORIDE[1]

BY JACOB CORNOG AND R. A. KARGES

I. Preparation

Old Method.—Iodine monochloride has usually been prepared by leading chlorine over solid iodine.[2] The crude product thus obtained was distilled; the portion of the distillate forming between 100 and 102° was retained. The distillate was far from pure. Stortenbecker[3] obtained iodine monochloride of good quality by repeatedly recrystallizing the distillate in its own mother liquor.

Improvement of the Old Method.—The present authors found that passing a slow stream of chlorine through the system during distillation and collecting the distillate formed between 100 and 101.5° increased the yield from about 35 to about 85% and also improved the quality of the

[1] From a thesis submitted to the Graduate College of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy, by R. A. Karges, August, 1931.

[2] Gay-Lussac, *Ann. chim.*, **91**, 1 (1814); Serullas, *Ann. chim phys.*, **22**, 180 (1833); Harmay, *J. Chem. Soc.*, **26**, 815 (1873); *ibid.*, **35**, 269 (1879); Thorpe, *ibid.*, **37**, 174 (1880); **61**, 925 (1892).

[3] Stortenbecker, *Rec. trav. chim.*, **7**, 152 (1888).