mentally as have the specific heat, freezing point and heat of dilution of solutions of calcium thiosulfate of various strengths. The solubility of calcium sulfite dihydrate and its specific heat have also been measured. Using these and other data, the free energy of formation, $\Delta F_{298}°$ of the thiosulfate ion has been calculated to be —125,110 calories.

BERKELEY, CALIFORNIA

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

THE CATALYTIC COMBINATION OF ETHYLENE AND HYDROGEN IN THE PRESENCE OF METALLIC COPPER

II. MEASUREMENTS OF REACTION VELOCITY AT 150°, 200° AND 250°

BY ROBERT N. PEASE

RECEIVED MAY 31, 1923

In a recent paper[1] the author has recorded results which indicate that the combination of ethylene and hydrogen in the presence of copper at 0° and 20° is, in its first stages, approximately monomolecular with respect to hydrogen, while ethylene in excess acts as an inhibitor. Grassi[2] has studied this reaction to some extent at temperatures between 150° and 275° and reports that in this region the reaction is bimolecular, as would be expected from the chemical equation. Grassi also found that the temperature coefficient between 150° and 275° was very small and decreased with rising temperature whereas between 0° and 20°, the author found the temperature coefficient to be in the neighborhood of 1.6 per 10°, which is of the same order as that for many uncatalyzed reactions. These marked differences in the characteristics of the reaction in the two temperature regions made it important to repeat a part of Grassi's work, especially as this investigator carried his determinations over only a small fraction of the total reaction.

The apparatus and method were the same as those used in the previous determinations at 0° and 20°, except that the temperature was maintained by means of an electrically heated air-bath. The copper catalyst in the state in which it was used for the runs at the lower temperature was much too active for use in the neighborhood of 200°. Partial de-activation was accomplished by heating it to 500–550° in a vacuum. During this treatment, the catalyst shrank about 15% of its original apparent volume and turned from a dirty red-brown to a salmon pink.

Reaction Velocity at 200°

The catalyst in the latter stage of activity was used for a series of runs at 200°. The results of this series, which are shown graphically in Figs. 1 and 2, indicate that the reaction is not exactly bimolecular as Grassi

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[1] Pease, THIS JOURNAL, 45, 1196 (1923).

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

states, though it approximates to this. For a bimolecular reaction, Curve I for the 50% mixture should lie to the left of the other two, as it does, in accordance with the principle that for a bimolecular reaction the velocity is a maximum with such a mixture. The other two curves, corresponding to 2:1 mixtures, should coincide. Actually, the velocity appears to be somewhat greater when hydrogen is in excess.

The decrease in pressure when hydrogen is in excess, is probably due in part to the solution of hydrogen in the copper. It is certain that the copper was able to take up some hydrogen, as was shown by measurements at 200°

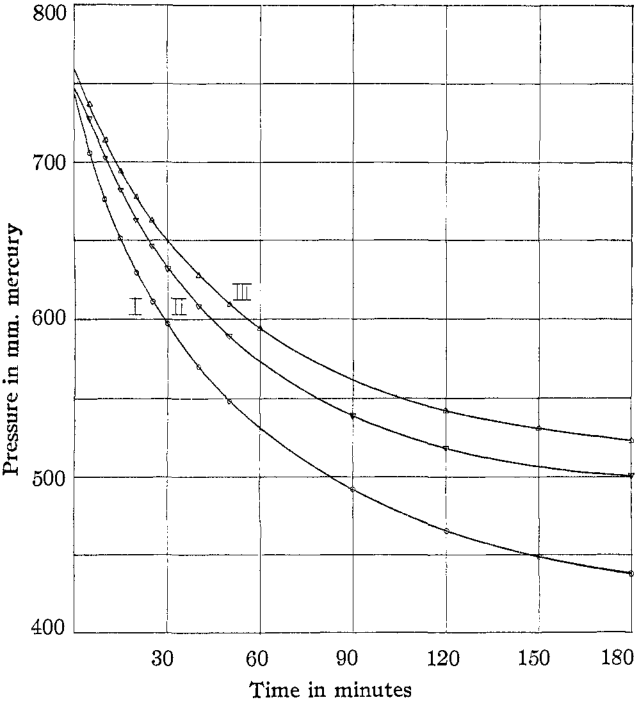

Fig. 1.—Reaction velocity at 200°, with initial pressure of 1 atmosphere. Curve I, 50% mixture, Run 105,[⊙]; Curve II, $2H_2-1C_2H_4$, Run 110,[▽]; Curve III, $1H_2 - 2C_2H_4$, Run 108,[△]

of pressure against volume with pure hydrogen. After each addition of gas there was a slow "drift" in the pressure, lasting sometimes for hours, and the total hydrogen in the bulb at any pressure was distinctly greater than that of either helium or ethylene. (These two gases gave the same results within experimental error, indicating that only minimal amounts of ethylene are adsorbed.) While it is impossible to state with certainty that this hydrogen was dissolved and not adsorbed, everything points to this. Previous heat treatments had caused marked decreases in the adsorption at 0° so that even at this temperature only a small adsorption was to be expected, and at 200° this must have been reduced to negligible proportions, if adsorption decreases with increasing temperature as is usually assumed. Nevertheless at 0.5 atmosphere and 200°, 1.0 cc. of hydrogen was taken up. This is as much as the same catalyst in a tremendously more active state took up at 0°. Furthermore, if this hydrogen is all adsorbed, it is adsorbed in many times greater quantity than ethylene.

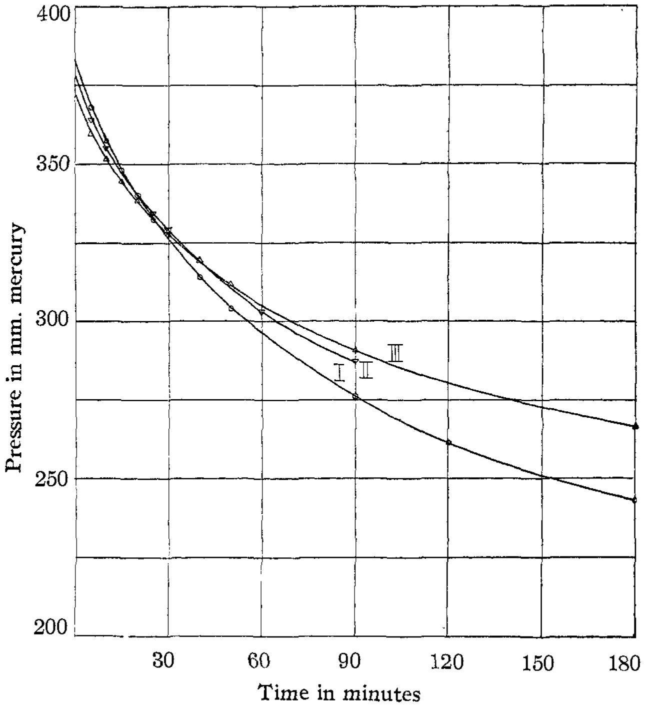

Fig. 2.—Reaction velocity at 200°, with initial pressure of 0.5 atmosphere. Curve I, 50% mixture, Run 106,[⊙]; Curve II, $2H_2 - 1C_2H_4$, Run 111,[▽]; Curve III, $1H_2 - 2C_2H_4$, Run 109,[△]

This would lead one to expect a marked influence on the reaction velocity, when none is found.

Reaction-velocity measurements were carried out with 50% mixtures and mixtures containing 2 volumes of one gas to 1 volume of the other, each at initial pressures of 0.5 and 1 atmospheres. To determine how the reaction velocity varies with the hydrogen and ethylene concentrations, the decreases in pressure in millimeters of mercury from the 5th to the 15th minute (ΔP) have been compared with the initial volumes of each of the gases in the bulb. Thus, in one experiment there were 4.14 cc. of hydrogen and 8.10 cc. of ethylene, while ΔP was 15.0 mm. In another there were 8.33 cc. of hydrogen and 4.17 cc. of ethylene, while ΔP was 16.5 mm. Again, in one experiment there were 8.52 cc. of hydrogen and 16.65 cc. of ethylene, while ΔP was 42.0 mm. In another, there were 16.65 cc. of hydrogen and 8.33 cc. of ethylene, while ΔP was 46.0 mm. It is seen that for the same amounts of 2:1 mixtures, the velocity is nearly the same whether hydrogen or ethylene is in excess, although an excess of hydrogen seems to correspond to a slightly greater velocity, as already mentioned. A comparison of reaction velocities when the amount of one gas is the same and the other is varied indicates, however, that a simple proportionality does not exist between gas concentration and reaction velocity. Thus, in two of the experiments, there were 8.10 cc. and 8.33 cc. of ethylene, respectively, while the volumes of hydrogen were 4.14 cc. and 16.65 cc. The corresponding reaction velocities were 15.5 mm. and 46.0 mm. The volumes of hydrogen stand in the ratio of 1:4.0, while the reaction velocities stand in the ratio of 1:3.0. In two other experiments the volumes of hydrogen were 8.33 cc. and 8.52 cc., respectively, while the volumes of ethylene were 4.17 cc. and 16.65 cc. The corresponding reaction velocities were 16.5 mm. and 42.0 mm. The volumes of ethylene stand in the ratio of 1:4.0 while the ratio of reaction velocities is 1:2.5. If it is assumed that the relation between reaction velocity and concentration can be expressed by $(\mathrm{d}p/\mathrm{d}t) = k \cdot V_{H_2}^{a} \cdot V_{C_2H_4}^{b}$, these relationships would give a = 0.80 and b = 0.66. The reaction velocity seems to vary not as the first power of the concentrations but as the 0.8 power of the hydrogen concentration and the 0.66 power of the ethylene concentration. If it is assumed that reaction velocity is directly proportional to the product of the amounts of the two gases adsorbed, the adsorptions of the gases should vary with these same fractional exponents of the pressure.

The results of calculations of the velocity constant, k in the equation $(\mathrm{d}p/\mathrm{d}t) = k \cdot V_{H_2}^{0.80} \cdot V_{C_2H_4}^{0.66}$, are given in Table I. The values of ΔP, the decrease in pressure from the 5th to the 15th minute, were substituted for $\mathrm{d}p/\mathrm{d}t$ and the initial volumes of hydrogen and ethylene for V_{H_2} and $V_{C_2H_4}$. Values of K were then calculated. $k = \Delta P/(V_{H_2}^{0.8} \cdot V_{C_2H_4}^{0.66})$. It is seen that the constants agree reasonably well.

TABLE I

THE VELOCITY CONSTANT AT 200°

Run No.	105	106	108	109	110	111	112
V_{H_2}	12.31	6.38	8.52	4.14	16.65	8.33	12.48
$V_{C_2H_4}$	12.31	6.37	16.65	8.10	8.33	4.17	12.57
ΔP	54.5	20.0	42.0	15.0	46.0	16.5	50.0
K	1.4	1.3	1.2	1.2	1.2	1.2	1.3

It has already been mentioned that no measurable amount of ethylene is adsorbed at 200° and that it is very doubtful if hydrogen is, either.

Under these circumstances, it is not surprising to find that the reaction approximates more nearly to what one would expect, namely, a bimolecular reaction. The reaction at 0° was found to be approximately monomolecular with respect to hydrogen and to be partially inhibited by ethylene. This latter could be traced to the marked adsorption of ethylene by the catalyst. In the absence of such marked adsorption at 200°, no such effect would be expected and none is found.

Temperature Coefficient

Grassi[2] found that for equal initial concentrations (not pressures) of 50% mixtures, the initial decreases in pressure in each 10-minute interval at 150°, 200°, 250°, and 275° were 2.2, 10.7, 12.8, and 14.0 mm., respectively. When these are corrected for temperature, and 200° is taken as the standard, they become 2.4, 10.7, 11.6, 12.1 mm. Since the concentrations are the same, the velocity constants are directly proportional to the above corrected pressure decreases. These correspond to a very small and continuously decreasing temperature coefficient.

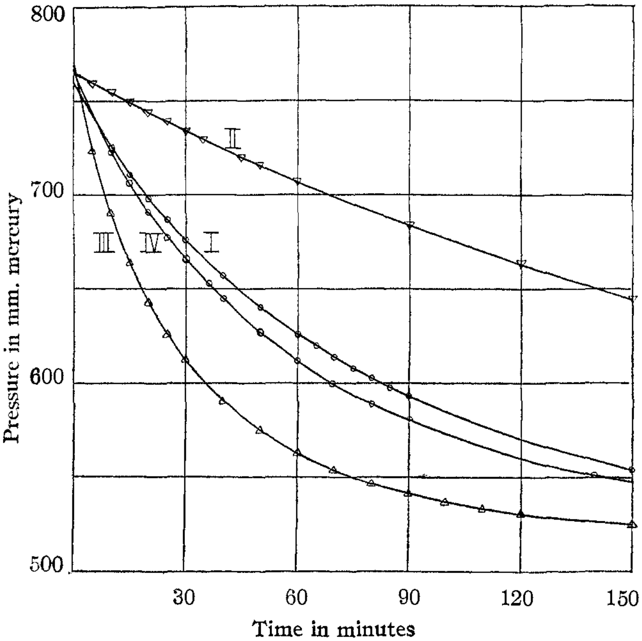

Fig. 3.—Reaction velocity at 150°, 200° and 250°, initial pressure of 1 atmosphere.—Mixture of $2C_2H_4 - 1H_2$. Curve I, velocity at 200°, Run 116, [⊙]; Curve II, velocity at 150°, Run 117, [▽]; Curve III, velocity at 250°, Run 118, [△]; Curve IV, velocity at 200°, Run 119, [⊙]

For comparison with Grassi's results, the author measured the reaction velocity at 150°, 200° and 250°. In these experiments a mixture of 1 volume of hydrogen to 2 volumes of ethylene was used, as it was thought that there would be less interference due to solution of hydrogen with such a mixture. The results of these measurements are shown graphically in Fig. 3. In Table II are given values of k calculated by the same relation as before, namely, $k = \Delta P/(V_{H_2}^{0.8} \cdot V_{C_2H_4}^{0.66})$. The values of ΔP have been corrected for temperature. The volumes are those at 0° and 760 mm.

TABLE II

REACTION VELOCITY AT 150°, 200° AND 250°

Run No.	Temp. °C.	V_{H_2}	$V_{C_2H_4}$	ΔP	k	$\Delta k/_{10°}$	ΔP(Grassi)	$\Delta k/_{10°}$
116	200	8.40	16.79	36.5	1.05	1.31	10.7	1.35
117	150	9.30	18.60	11.2	0.27		2.4	
118	250	7.67	15.35	53.8	1.74	1.15	11.6	1.02
119	200	8.32	16.63	30.0	0.85		(10.7)	

Unfortunately, there was a noticeable decrease in activity during these runs. This has been taken into account in calculating temperature coefficients.

For comparison, the values of ΔP from Grassi's results are given. These correspond directly to velocity constants, since the gas concentrations were made the same at the different temperatures. It will be seen that between 150° and 200°, the temperature coefficients of reaction velocity calculated from the two sets of results are in good agreement (1.31 and 1.35). Between 200° and 250°, the author's results give a distinctly higher coefficient than do those of Grassi, (1.15 and 1.02). Both sets agree, however, in assigning a very small and continuously decreasing coefficient to the reaction. The decrease in temperature coefficient between the 150–200° regions and the 200–250° regions is abnormally large even with the authors' values. On the basis of the Arrhenius equation, $\log \frac{k_2}{k_1} = \frac{A}{4.57} \cdot \frac{T_2 - T_1}{T_1 \cdot T_2}$, there is a normal decrease with increasing temperature if A, the so-called "heat of activation," is regarded as constant. The observed values of k are not in agreement with this assumption, however, the calculated values of A being 10800 cal. between 150° and 200° and 7000 cal. between 200° and 250°. As an explanation of the anomalous result just mentioned, the decrease in the adsorptive power of the contact mass with increasing temperature suggests itself. The active masses in a contact catalytic action are functions of the amounts of reactants adsorbed. In comparing reaction rates at two temperatures, the comparison should therefore be made at such gaseous concentrations that equal amounts of reactants are adsorbed at the two temperatures. Actually, comparisons are made at equal gaseous concentrations, corresponding to continuously decreasing adsorptions, or surface concentrations, with increasing temperature. This leads to temperature coefficients (and heats of activation) smaller than the true ones corresponding to the reaction on the surface and continuously decreasing, unless the adsorption is a linear function of the temperature. The observed temperature coefficient is composite of two effects, namely, the true positive coefficient of the surface action and the negative coefficient of adsorption. In the present case the adsorptions at the temperatures in question were not measurable in the case of ethylene and are of doubtful significance in the case of hydrogen, so that no such correction can be made. That the adsorption of ethylene by copper does decrease markedly through a part of the temperature region is shown by the results of Taylor and Burns,[3] who found that the adsorption at 1 atmosphere on a particular sample of copper was 0.65 cc. at 110° and not measurable at 218°. Experiments are at present in progress to determine the temperature coefficients of adsorption of ethylene and hydrogen on active copper between 0° and 200°.

Although the absolute reaction velocities in the experiments at 0° and 20° already reported are not directly comparable with those just given because of the enormous difference in catalytic activity, it might be expected that the temperature coefficients of reaction velocity (and the heats of activation) might be compared. The velocity constants at 0° and 20° were 0.50 and 1.32 in the particular units chosen, leading to a temperature coefficient of 1.62 per 10° and a heat of activation of 7700 cal., a value which lies between the two obtained at the higher temperatures (10,800 cal. and 7000 cal.). Since the adsorption of hydrogen at 0° and 20°, upon which the reaction appears to depend in this region, was the same, one would have expected that the temperature coefficient and heat of activation in this temperature region would have been the true one for the surface action on the basis of the argument already given. In this case a value for the heat of activation considerably larger than that at the higher temperature was to have been expected instead of an intermediate value. Perhaps further discussion may best be postponed until more results have been accumulated. It is of interest, however, to find that the heats of activation for the reaction in the presence of the copper catalyst in two such different states of activity are of the same order.

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

Summary

Measurements of the velocity of combination of hydrogen and ethylene in the presence of copper at 150°, 200° and 250° have shown that in this temperature region the reaction is more nearly bimolecular, in contrast to the combination at 0°, at which temperature the reaction is approximately monomolecular with respect to hydrogen and inhibited partially by excess

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

of ethylene. The more nearly normal character of the reaction at the higher temperatures is believed to be due to the fact that under these circumstances the reacting gases are not measurably adsorbed by the catalyst. The temperature coefficient is much smaller at the higher temperature and is decreasing. By taking into account the decrease of adsorption with rise in temperature as well as the normal increase in velocity of the surface reaction, these facts have been accounted for qualitatively.

University, Virginia

[Contribution from the Cobb Chemical Laboratory of the University of Virginia]

THE KINETICS OF THE CONVERSION OF CREATINE INTO CREATININE IN HYDROCHLORIC ACID SOLUTIONS

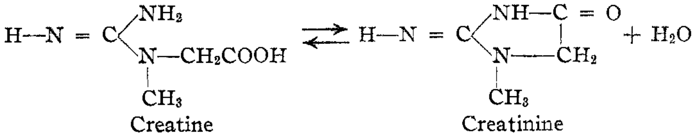
By Graham Edgar and R. A. Wakefield

Received June 4, 1923

Introduction

The literature contains numerous references to the conversion of creatine into creatinine in the presence of acid catalysts. Practically all of these investigations have either been purely qualitative in nature, or have been concerned with determining the conditions under which the reaction goes to completion, in order to permit the quantitative estimation of creatine (as creatinine) by the colorimetric method of Folin.[1]

The reversible reaction



$$\mathrm{H{-}N = C}\begin{cases}\mathrm{NH_2}\\ \mathrm{N{-}CH_2COOH}\\ \ \,|\\ \ \mathrm{CH_3}\end{cases} \rightleftharpoons \mathrm{H{-}N = C}\begin{cases}\mathrm{NH{-}C = O}\\ \quad\ \ |\\ \mathrm{N{-}{-}CH_2}\\ \ \,|\\ \ \mathrm{CH_3}\end{cases} + \mathrm{H_2O} \qquad (1)$$

Creatine → Creatinine

is of great interest in biochemistry, as it occurs in the normal and abnormal processes of the metabolism; it is also of interest from the theoretical standpoint, as it represents a type of reaction catalyzed by acids to which less attention has been paid than those of ester hydrolysis and similar reactions. The present paper represents a brief study of the kinetics of the reaction in the presence of hydrochloric acid as a catalyst.

Experimental Methods

Materials.—Commercial creatine of very good quality was purified by two crystallizations from water, and was allowed to dry in the air. The product was pure white, odorless, and finely crystalline. Other reagents used were commercial c. p. products.

As analytical standards pure creatinine picrate[2] and creatinine zinc chloride were employed.

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[1] Folin, *Am. J. Physiol.*, **13**, 48 (1905).

[2] Edgar, *J. Biol. Chem.*, **56**, 1 (1923).