mum may be due to poisoning of the catalyst by the small quantity of amine formed during the exchange, and the plateau at higher concentrations may be due to appreciable adsorption of the nitro compound which would displace the amine.

TABLE II

THE EXCHANGE OF DEUTERIUM GAS OVER RANEY NICKEL CATALYST WITH CERTAIN METHANOL SOLUTIONS

Concn., mole/l.	% ex. g.$^{-1\,a}$	Concn., mole/l.	% ex. g.$^{-1\,a}$
0 (pure MeOH)	71.1^{b}	β-Nitrostyrene	
Nitromesitylene		0.0129	47.8
0.0134	40.4	.0587	14.1
.0198	48.1	.0971	7.36
.0454	65.6	.1553	0
.0454	63.7	.2279	0
.0705	64.5	Nitrobenzene	
.0935	60.8	0.0257	17.7
.0992	57.5	.0514	11.5
.1674	60.8	.0771	0
.2710	63.7	.1285	0
.2710	67.2	2-Nitro-1-butene	
.2710	63.2	0.0169	19.2
Nitroethane		.0338	0
0.0340	35.3	.0676	0
.0680	19.4		
.1020	4.34		
.1360	0		

[a] For 10 minutes reaction time. [b] Average of seven determinations, each representing three analyses.

Discussion

The kinetic behavior of the catalytic hydrogenation of nitro compounds in ethanol solution over Raney nickel catalyst is first order with respect to hydrogen pressure and zero order with respect to the hydrogen acceptor. This is found for both aromatic and aliphatic nitro compounds, and is in contrast to the behavior over platinum catalyst with acetic acid solvent. In the latter case, the hydrogenation of the aromatic nitro compounds is also first order with respect to hydrogen pressure and zero order with respect to the nitro compound; but for nitroparaffins, the kinetic behavior is reversed, in that the reduction is zero order with respect to the hydrogen pressure and first order with respect to the acceptor.

The exchange experiments with deuterium gas and acetic acid in the presence of platinum and with deuterium gas and methanol in the presence of Raney nickel reflect these differences. In the first situation, aromatic nitro compounds when added in small quantities prevent the exchange,[2] while aliphatic nitro compounds do not.[3] For experiments with deuterium gas and methanol over nickel, both aliphatic and aromatic nitro compounds prevent the exchange. Thus, both hydrogenation and exchange experiments indicate strong adsorption of both nitroparaffins and aromatic nitro compounds on the nickel surface. Presumably these, when present in appreciable concentrations, exclude the methanol from the catalyst surface, thus preventing the exchange reaction.

The situation occurring with nitromesitylene is unusual, in that it does not prevent the exchange. It is well known that the methyl substituents prevent resonance between the nitro group and the benzene ring, and this influences such properties as dipole moments[11] and Raman spectra,[12] thus making the compound behave somewhat more as a nitroparaffin than as an aromatic nitro compound. This is evidenced in the hydrogenation of nitromesitylene over platinum in acetic acid solution.[7] However, since nitroparaffins and aromatic nitro compounds influence the exchange of deuterium with methanol over Raney nickel, one would expect that the nitromesitylene would suppress the exchange reaction. The reason for its behavior is not clear unless there may be some unexpected exchange of deuterium with the nitromesitylene itself.

Acknowledgment.—The authors are indebted to the United States Atomic Energy Commission for support of this work.

[11] F. Brown, J. M. A. deBruyne and P. Gross, THIS JOURNAL, **56**, 1291 (1934).

[12] R. H. Saunders, M. J. Murray and F. F. Cleveland, *ibid.*, **63**, 3121 (1941).

KNOXVILLE, TENN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, FACULTY OF LIBERAL ARTS AND EDUCATION, MIYAZAKI UNIVERSITY, MIYAZAKI CITY, MIYAZAKI, JAPAN]

Studies on the Mechanism of Clemmensen Reduction. I. The Kinetics of Clemmensen Reduction of *p*-Hydroxyacetophenone

BY TADAAKI NAKABAYASHI*

RECEIVED AUGUST 26, 1959

The kinetics of the reduction of *p*-hydroxyacetophenone with zinc amalgam and hydrochloric acid has been studied at 60°. Except in the initial stage, the reaction is first order with respect to the ketone. Chloride ion and zinc concentration have a predominant effect on the rate, whereas the effect of the potential of the zinc amalgam or hydrogen ion concentration is small. The effect of polyvinyl alcohol on the rate and on the potential of zinc amalgam are reported. The apparent energy of activation of the reaction is 5.1 kcal./mole. A hypothesis on the mechanism of this reaction is presented.

Clemmensen reduction is widely employed in organic syntheses,[1] but the mechanism of the reaction is not yet established. The present work has been undertaken in order to solve this problem.

Steinkopf and Wolfram studied the Clemmensen reduction of benzophenone, acetophenone, esters of keto acids and benzaldehyde.[2] The mechanism

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[1] E. L. Martin, "Organic Reactions," Vol. 1, edited by R. Adams, John Wiley & Sons, Inc., New York, N. Y., 1942, p. 155.

[2] W. Steinkopf and A. Wolfram, *Ann.*, **430**, 113 (1923).

proposed by them is a stepwise reduction in which a radical $R\dot{C}OHR'$ and an alcohol $RCHOHR'$ are essential intermediates. Bradlow and VanderWerf compared the yields of diphenylmethanes with those of benzopinacols in the reduction of substituted benzophenones and proposed a mechanism according to which a radical $R\dot{C}OHR'$ formed from the carbonyl compound is reduced, according to the electronegativity of the substituents, to hydrocarbon or dimerizes to pinacol.[3] Brewster suggested that the carbonyl compound coördinates with the metal surface to form a carbon–metal bond or an oxygen–metal bond according to the constitution of the carbonyl compound or acidity of the reaction mixture.[4a,4b] Electron transfer and addition of proton follow thereafter. He interpreted some features of this reaction in terms of this hypothesis. Martin[5] and Leonard[6] gave brief discussions on the mechanism of this reaction, but these cannot be adopted as general.

In all of these studies carbonyl compounds were reduced by the ordinary method of Clemmensen reduction, in boiling hydrochloric acid with zinc amalgam for several hours. The mechanism of the reaction has been discussed from the results of analysis of the reaction products; little attention has, however, been paid to the course of this reaction. We have studied the course of this reaction by means of kinetics and other methods and found some features which have led to a new hypothesis on the reaction mechanism. In this paper will be reported the kinetics of the reaction of *p*-hydroxyacetophenone with liquid zinc amalgam and hydrochloric acid.[7] As few studies on the kinetics of reduction of organic compounds with metal have been reported, the study on the kinetics of Clemmensen reduction is also of interest from this point of view. *p*-Hydroxyacetophenone was employed as substrate, because it is reduced to *p*-ethylphenol by Clemmensen's method in good yield[8] and is soluble in water.

Results

Material Balance of the Reaction.—Since Clemmensen reduction is often accompanied by side reactions, *i.e.*, formation of pinacol, olefin and the like, the material balance of the reduction of *p*-hydroxyacetophenone first was examined. It became clear in the preliminary experiments that *p*-hydroxyacetophenone is almost quantitatively (more than 90%) reduced to *p*-ethylphenol under the conditions: 0.5–3 *N* hydrochloric acid, 2% concentration of zinc in the amalgam, 60°, nitrogen atmosphere. The velocity of hydrogen evolution is small compared to that of the reduction. It also became clear that *p*-ethylphenol is formed in good yield (some 90%) when the reaction is carried out at 60° with sulfuric acid and zinc amalgam or with hydrochloric acid and unamalgamated zinc. The yield of *p*-ethylphenol, however, decreases as the concentration of zinc in the amalgam decreases.

The material balance of the reaction shows that the reduction product other than *p*-ethylphenol is that corresponding to two-electron reduction of *p*-hydroxyacetophenone. From results which will be described later,[9] it is presumably *p*-hydroxystyrene or its polymer.

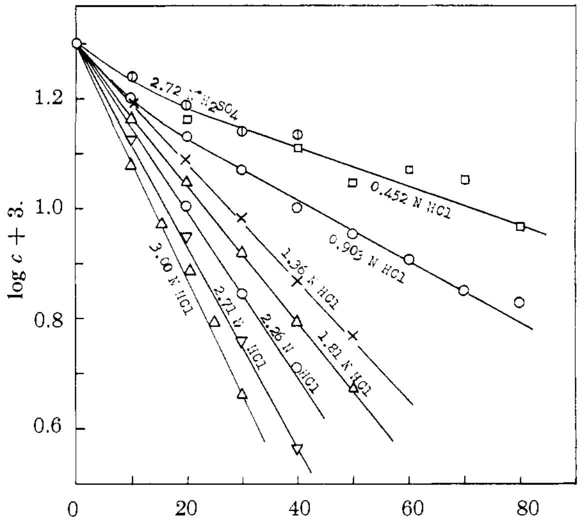

Fig. 1.—The rate of the reduction of *p*-hydroxyacetophenone in hydrochloric acid; 2.03% Zn–Hg, 60°.

TABLE I

THE EFFECT OF ZINC CONCENTRATION ON THE MATERIAL BALANCE OF THE REACTION[a]

Concn. of Zn, %	Time of reacn., min.	Reaction, %	Reaction products, mole % based on the reacted *p*-OHC_6H_4Ac H_2	*p*-Ethylphenol	$ZnCl_2$	n[b]
0.105	120	56.4	11.9	34.7	150.7	1.06
.191	70	61.4	6.8	46.0	150.8	0.96
.522	50	66.0	5.5	68.9	176.0	1.05
.886	30	65.3	3.5	79.2	186.0	1.16

[a] 2.00 *N* HCl, 0.02 mole./l. *p*-OHC_6H_4Ac, 60°. [b] $n = (ZnCl_2 - H_2 - p\text{-ethylphenol} \times 2)/(100 - p\text{-ethylphenol})$.

Reaction Velocity.—The logarithm of the concentration of *p*-hydroxyacetophenone (c) is plotted against time (t) in Fig. 1. The volume of the *p*-hydroxyacetophenone solution in hydrochloric acid (13.3% aqueous ethanol was employed as solvent) was 59.2 ml., that of zinc amalgam 30 ml. and the contact area of the two phases was 23 cm.^{2}.[10] The aqueous layer was stirred at a constant rate.[11] Initial concentration of *p*-hydroxyacetophenone (c_0) was 2×10^{-2} mole/l., that of hydrochloric acid 0.452–3.00 *N*, that of zinc amalgam 2.03% (4.06 moles/l.) and temperature 60°. The result in the case of 2.72 *N* sulfuric acid also is shown. When the concentration of hydrochloric acid is higher than 2.15 *N*, the reaction is first order with respect to *p*-hydroxyacetophenone from the beginning of the reaction. When the initial concentration of *p*-hydroxyacetophenone is low, or when the concentration of hydrochloric acid is lower than 1.81 *N*, the reaction rate is somewhat higher initially than required by first-order kinetics but thereafter conforms to first-order kinetics. Therefore, the apparent first-order velocity constants were calculated by the least squares method from the results 5–10 min. after the beginning of the reaction. As shown in Table II, c_0 has little effect on the first-order rate constant, showing that this reaction is of first order with respect to *p*-hydroxyacetophenone. The reaction rate measured in sulfuric acid is much smaller than that in hydrochloric acid of the same hydrogen ion concentration.

The Effect of Polyvinyl Alcohol on the Rate of the Reaction.—The fact that, in certain cases, the rate of the reaction is somewhat greater than that expected from the first-order rate equation may be regarded as a surface-chemical phenom-

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(3) H. L. Bradlow and C. A. VanderWerf, THIS JOURNAL, **69**, 1254 (1947).

(4) (a) J. H. Brewster, *ibid.*, **76**, 6361 (1954); (b) **76**, 6364 (1954); (c) J. H. Brewster and other workers, *ibid.*, **76**, 6368 (1954).

(5) E. L. Martin, *ibid.*, **58**, 1438 (1936).

(6) N. J. Leonard and other workers, *ibid.*, **71**, 3089 (1949).

(7) (a) T. Nakabayashi and K. Kai, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **76**, 1332 (1955); (b) T. Nakabayashi and K. Kai, *ibid.*, **77**, 657 (1956).

(8) E. Clemmensen, *Ber.*, **47**, 51 (1914).

(9) Part II of this series, p. 3906.

(10) Values at room temperature.

(11) These conditions were employed throughout this work.

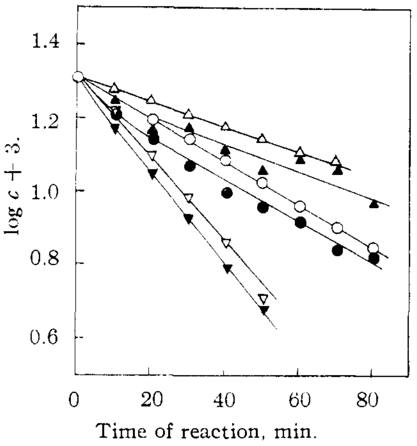

Fig. 2.—The effect of polyvinyl alcohol on the rate of the reduction of *p*-hydroxyacetophenone: △, 0.452 *N* HCl, P.V.A. 0.008%; ▲, no P.V.A.; ○, 0.904 *N* HCl, P.V.A. 0.008%; ●, no P.V.A.; ▽, 1.81 *N* HCl, P.V.A. 0.008%; ▼, no P.V.A., 2.03% Zn-Hg, 60°.

TABLE II

THE EFFECT OF c_0 ON THE FIRST-ORDER RATE CONSTANT k

Concn. of HCl, *N*	$c_0 \times 10^2$, moles/l.	$k \times 10^2$, min.$^{-1}$	Concn. of HCl, *N*	$c_0 \times 10^2$, moles/l.	$k \times 10^2$, min.$^{-1}$
2.15	1.99	3.26	2.72	1.99	4.03
2.15	1.19	3.36	2.72	0.798	4.21
2.26	3.98	3.40			
2.26	2.05	3.57			

enon similar to the "maximum" observed in polarography. Polyvinyl alcohol was added, therefore, to the reaction mixture as a maximum suppressor.[12] The effect of polyvinyl alcohol on the rate of the reaction is shown in Fig. 2. The reaction is considerably suppressed at the beginning by the addition of 0.008% polyvinyl alcohol with the result that the reaction follows first-order kinetics from the beginning of the reaction. This effect of polyvinyl alcohol is also observed in the reduction of acetophenone, nitrobenzene and *p*-nitrophenol with zinc amalgam and hydrochloric acid.[7b] In these cases the rate of initial stage of the reaction is greatly suppressed by 0.008–0.17% polyvinyl alcohol, but the later stage to which the first order-rate equation applies is only slightly affected by it (Fig. 3). The anomaly in the reaction rate observed in the absence of polyvinyl alcohol may thus be regarded as a kind of unstable surface-chemical phenomenon which disappears on the addition of a surface active substance such as polyvinyl alcohol. Therefore, the initial rapid reaction may be regarded as a result of, say, eddy currents near the surface of the amalgam which have been suggested to be responsible for the "maximum" observed in polarography.[13] Thus the procedure of calculating the first-order rate constant excluding the initial period may be justified.

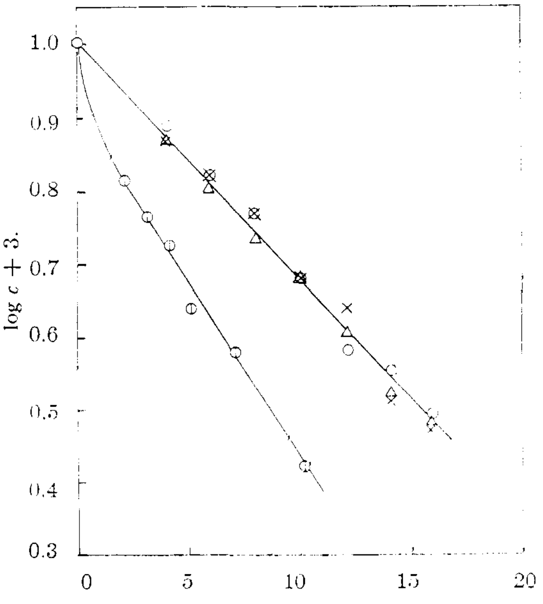

Fig. 3.—The effect of polyvinyl alcohol on the rate of the reduction of acetophenone; 1.81 *N* HCl, 2.03% Zn-Hg, 60°: ⦶, no P.V.A.; △, 0.008%; ×, 0.08%; ○, 0.16%.

The Effect of Potassium Chloride on the Rate of the Reaction.—In hydrochloric acid of the concentrations mentioned above, the activity coefficients of hydrogen and chloride ion are considerably affected by the concentration of the acid. Potassium chloride was added, therefore, to the solution to make the total concentration of electrolytes constant for all the range of hydrochloric acid concentration studied. The effect of hydrochloric acid concentration on the rate of reaction was examined keeping the concentration of chloride ion constant at 3.00 and 2.00 *N*, respectively. Figure 4 shows the effect of hydrochloric acid concentration on the rate constant in the presence and absence of potassium chloride. When the concentration of chloride ion is kept constant by adding potassium chloride and sufficient hydrochloric acid is present, the apparent rate constant is only slightly affected by the concentration of the acid. But it is markedly affected by hydrochloric acid concentration when the latter becomes less than one-third of the total chloride ion concentration.

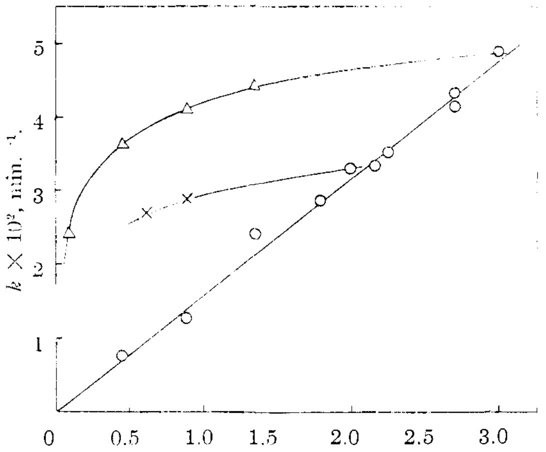

Fig. 4.—The effect of hydrochloric acid concentration on the rate of the reaction; 2.03% Zn-Hg, 60°: ○, HCl; △, [HCl] + [KCl] = 3.00 *N*; ×, [HCl] + [KCl] = 2.00 *N*.

As the total concentration of electrolytes is sufficiently high compared to the concentration of *p*-hydroxyacetophenone, ionic strength may be regarded as constant throughout the reaction. Moreover, the effect of hydrochloric acid concentration on the activity coefficient of hydrogen ion may be comparatively small because the total concentration of electrolytes is kept constant. This means that chloride ion takes part in the rate-determining step. In view of the effects of chloride and hydrogen ion on the rate shown in Fig. 4, two mechanisms may be possible for this reaction

$$A + H_3O^+ \rightleftharpoons AH^+ \qquad \text{(a) fast}$$
$$AH^+ + Cl^- + (Zn) \longrightarrow B \qquad \text{(b) slow}$$
$$A + Cl^- + (Zn) \rightleftharpoons X \qquad \text{(a') slow}$$
$$X + H_3O^+ \longrightarrow B \qquad \text{(b') fast}$$

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(12) J. Ukita and other workers, *Chem. High Polymers (Japan)*, **11**, 176 (1954).

(13) M. v. Stackelberg and other workers, *Z. Elektrochem.*, **44**, 663 (1938).

where A is *p*-hydroxyacetophenone, X the intermediate and B the product. If the equilibrium constant K of step a is so large that a major part of A is converted into AH^+, the velocity of step b may become independent of hydrogen ion concentration. But K must be of the order of 10 or more for this to occur, and this is not the case for *p*-hydroxyacetophenone. Mechanism a–b cannot be adopted here for this reason. The alternate mechanism a′—b′, however, is able to account for the kinetic behavior, at least qualitatively. In the first place, a slow and reversible step in which chloride ion (probably together with zinc, for the reaction of *p*-hydroxyacetophenone with chloride ion alone may be impossible) reacts with *p*-hydroxyacetophenone takes place, followed by a fast step involving hydrogen ion which may, as the concentration of hydrogen ion decreases, affect the reaction velocity. The rate constant measured in 2.72 N sulfuric acid is approximately one tenth that in hydrochloric acid of the same hydrogen ion concentration. Since the difference in reaction velocity is too large to be ascribed to the difference in activity of hydrogen ion in these two solutions, it may be concluded that the reaction velocity varies with the kind of anions. Furthermore, as will be described later, the relationship between electrode potential of the zinc amalgam and the time of reaction in this case is quite different from that in the case of hydrochloric acid.

The Effect of Zinc Concentration in the Amalgam.—The effect of zinc concentration on the rate was studied under the following conditions: hydrochloric acid 2.00 N, c_0 2.0 × 10^{-2} mole/l., zinc concentration 0.105% (0.217 mole/l.)–2.03% (4.06 moles/l.), 60°. As already stated, the yield of *p*-ethylphenol decreases as the zinc concentration in the amalgam decreases, *p*-hydroxystyrene or its polymer being produced in this case. The over-all rate constant including both formation of *p*-ethylphenol and of *p*-hydroxystyrene is regarded as the rate constant of Clemmensen reduction of *p*-hydroxyacetophenone. The result is shown in Fig. 5. The apparent rate constant is approximately proportional to the 0.6 power of zinc concentration.

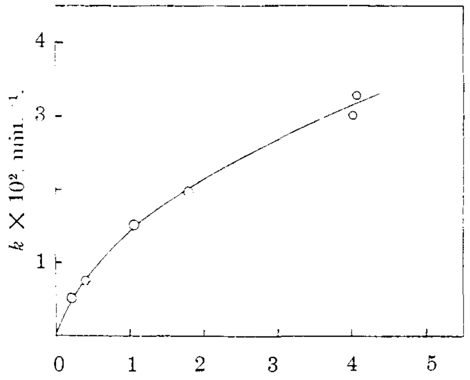


Fig. 5.—The effect of zinc concentration on the rate of the reaction: 2.00 N HCl, 60°

The Energy of Activation.—Figure 6 shows the effect of reaction temperature (30–72°) on the rate. Initial concentrations are: hydrochloric acid 2.00 N, zinc amalgam 2.00%, c_0 2.0 × 10^{-2} mole/l. A plot of log k *vs.* $1/T$ gives a straight line from whose slope the apparent energy of activation of the reaction is calculated to be 5.1 kcal./mole.

The Electrode Potential of Zinc Amalgam.—The electrode potential of zinc amalgam was measured concurrently with reaction rate. The curve I of Fig. 7 shows a typical example of the results (hydrochloric acid 1.81 N, c_0 2.03 × 10^{-2} mole/l., 60°). The potential rises by some 0.1 v. at the beginning of the reaction, then gradually reaches a maximum and thereafter drops steadily. The potential drop from B to C is linear with respect to time; this period is called the stationary state for the present. The time required in the course of A to B is 3–15 min., and it becomes shorter as the concentration of hydrochloric acid or c_0 becomes higher. In some cases no linear part corresponding to the B–C line appears. Curve II (c_0 2.04 × 10^{-2} mole/l., 0.452 N hydrochloric acid + 2.55 N potassium chloride) and III (c_0 2.04 × 10^{-2} mole/l., 2.72 N sulfuric acid) in Fig. 7 are examples of these cases. The period corresponding to the part AB of the curve I, which is called non-stationary state for the present, is long enough to exclude the stationary state.

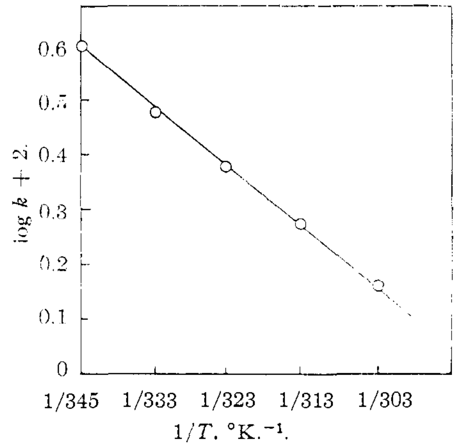


Fig. 6.—Change in rate with temperature: 2.00 N HCl, 2.0% Zn–Hg.

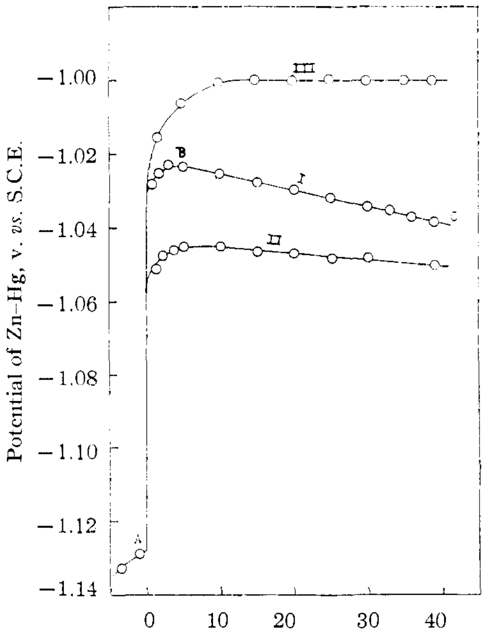


Fig. 7.—The electrode potential of Zn–Hg *vs.* time of reaction: c_0 = 0.02 mole/l., 2.03% Zn–Hg, 60°.

The stationary states in the relationships between the potential and the time observed in hydrochloric acid of various concentration are shown in Fig. 8. In general, the time required to reach the stationary state becomes shorter and $-dE/dt$ (the slope of the stationary state) larger as the concentration of hydrochloric acid increases. When the concentration of chloride ion is kept constant at 3.00 N, the relationships between potential and time give almost the same straight line within the range of 0.9–3 N hydrochloric acid, the stationary states being reached faster as hydrochloric acid becomes more concentrated. The effect of zinc concentration on the potential is shown in Fig. 9 (2.00 N hydrochloric acid, c_0 0.02 mole/l., 60°). The potential rises from −1.02 to −0.99 v. (S.C.E.) as the concentration of zinc in the amalgam decreases from 2.00 to 0.105%.

$-dE/dt$ increases with k, the first-order rate constant, and the former is almost proportional to the latter as pictured in Fig. 10. That is

$$-dE/dt = Bk$$

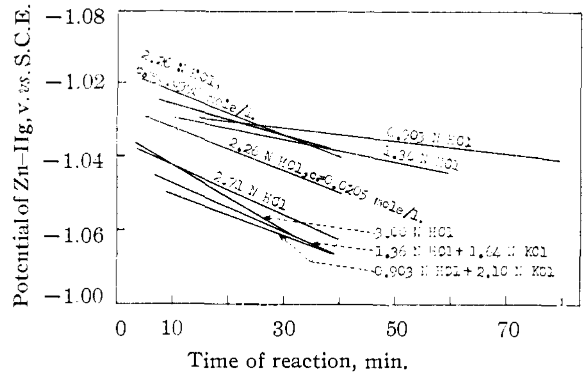


Fig. 8.—The stationary states: 2.03% Zn–Hg, c_0 = 0.02 mole/l., 60°.

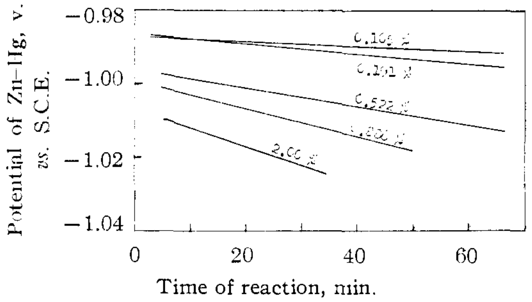


Fig. 9.—The effect of zinc concentration on the electrode potential of Zn–Hg: c_0 = 0.02 mole/l., 2.0 N HCl, 60°.

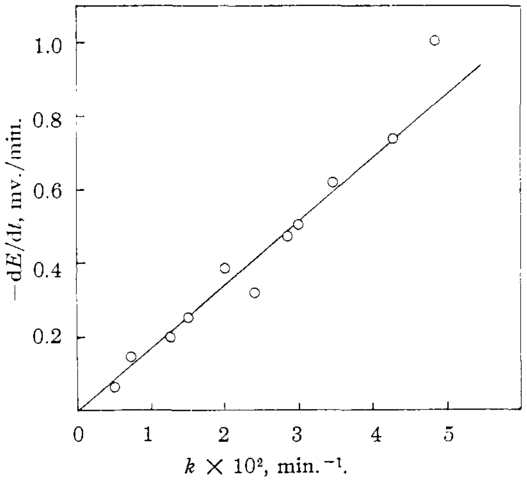


Fig. 10.—−dE/dt *vs.* k.

The mean value of the constant B is 16.6 mv. Introducing the rate equation, $-dc/dt = kc$, and integrating, we obtain

$$E = A + B \ln c$$

where A is the constant of integration. When c_0 is doubled keeping the concentration of hydrochloric acid constant at 2.26 N, the potential rises by 9.9 mv. as shown in Fig. 8. This potential rise roughly agreed with the calculated value, 11.1 mv., from the equation

$$\Delta E = B \ln c_2/c_1$$

Figure 11 shows the effect of polyvinyl alcohol on the potential of zinc amalgam. As shown in the figure, the potential-time relationship is quite different from that observed in the absence of polyvinyl alcohol. The potential-time relationship can be explained in terms of concentration polarization caused by the zinc ion produced in the course of the reaction.[7b]

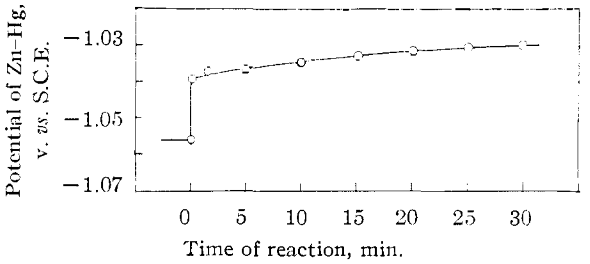


Fig. 11.—The electrode potential of Zn–Hg *vs.* time of reaction in the presence of polyvinyl alcohol: c_0 = 0.02 mole/l., 0.008% polyvinyl alcohol, 2.03% Zn–Hg, 60°.

Discussion

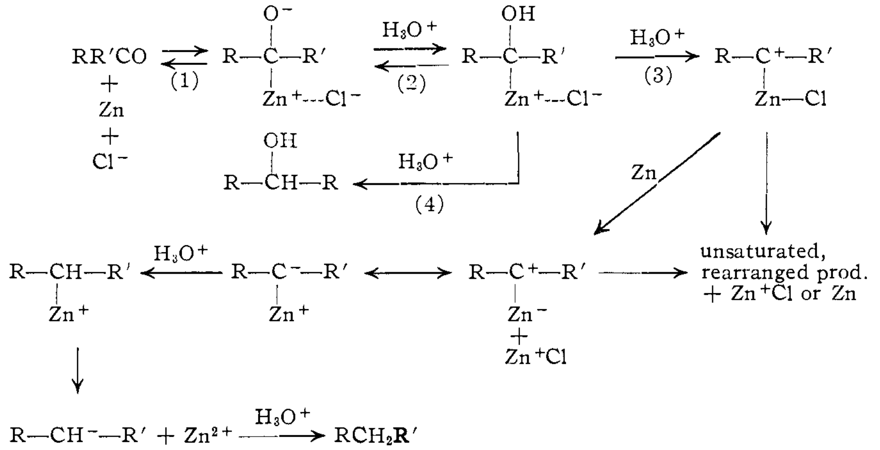
Brewster proposed a mechanism of Clemmensen reduction in which electrons are transferred to carbonyl compound through a bond formed between carbonyl–carbon or carbonyl–oxygen and metal.[4b] Adopting many features of this mechanism, the author presents this hypothesis on the mechanism of Clemmensen reduction. The results of the present experiments and some other features of this reaction will be discussed in terms of this hypothesis.

To begin with, the effect of the potential of zinc amalgam on the rate of the reaction will be discussed. As shown in Figs. 7, 8 and 9, the potential drops by 10–30 mv. in the course of the reaction. But no appreciable change in k is observed. Furthermore, when c_0 is doubled and consequently the potential rises by 10 mv., k decreases by no more than 3–5%. If the decrease in k is assumed to be caused by the rise in the potential of zinc amalgam, a 10–15% increase in k may be expected as the concentration of hydrochloric acid increases from 0.9 to 3.0 N because the potential of zinc amalgam drops from −1.03 to −1.06 v. (S.C.E.) in this case (Fig. 8). But this is not the case; k increases 4-fold as the concentration of hydrochloric acid increases from 0.9 to 3.0 N. This shows that the concentration of hydrochloric acid, *i.e.*, the concentration of chloride ion in this case, has the predominant effect on the reaction rate rather than the potential of zinc amalgam. Similarly it can be seen from the relationship between k and zinc concentration in the amalgam that zinc concentration has the predominant effect on the rate of reaction rather than the potential of zinc amalgam. This suggests that no process of electron transfer is involved in the rate-determining step of this reaction; the mechanism of this reaction is likely to be different from the electrochemical reduction such as

$$R + e^- \longrightarrow R^- \quad \text{slow} \qquad R^- + H^+ \longrightarrow RH \quad \text{fast}$$
$$R + H^+ \rightleftarrows RH^+ \quad \text{fast} \qquad RH^+ + e^- \longrightarrow RH \quad \text{slow}$$

where R is the substance to be reduced, RH a product or an intermediate of the reduction.

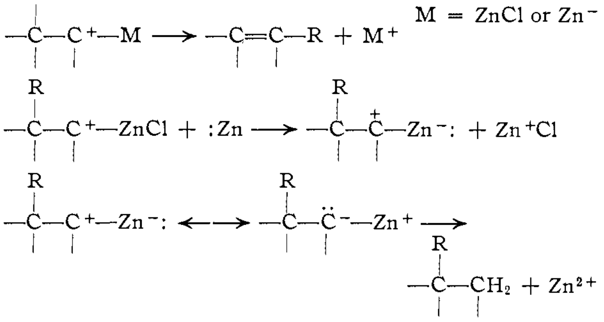
Kinetic study has shown that, in the presence of sufficient amount of hydrochloric acid, the rate of the reaction is almost independent of the concentration of hydrogen ion. So atomic hydrogen cannot be the reductant. Furthermore, if a reaction mechanism involving atomic hydrogen as an intermediate is assumed, the velocity of this reaction should be affected by the potential of the zinc amal-



gam because the discharge of hydrogen ion takes place according to the electrochemical mechanism.[14]

The kinetic behavior of this reaction is best understood, at least qualitatively, on the assumption that step 1 is the rate-determining step of this reaction followed by fast steps 2, 3 and 4; steps 3 and 4 become slow enough to affect the over-all rate of the reaction as the concentration of hydrogen ion decreases. Chloride ion assists the coördination of the carbonyl group to zinc by forming a bond with zinc and thus facilitating the charge separation accompanying the coördination. Sulfate ion is so bulky that the coördination of this ion to zinc is hindered, because this reaction takes place at the surface of the amalgam and hence is sensitive to steric effects.

As will be shown in part II of this series, the intermediate produced through these steps is supposed to be of the carbonium ion type. Unsaturated or rearranged products often found as by-products are formed from this intermediate; they are not formed through the dehydration of the corresponding alcohol. Brewster and co-workers reported that Clemmensen reduction of *t*-butyl phenyl ketone gives neopentylbenzene and 2-methyl-3-phenyl-2-butene but not 2-methyl-3-phenylbutane.[4c] Pinacolone gives neohexane and not rearranged products.[4c] These results suggest that the intermediate carbonium ion has comparatively little tendency to rearrange and the rearranged carbonium ion is not reduced further. The organometallic carbonium ion which was proposed by Brewster in an essentially similar formulation seems reasonable for an explanation of the above-mentioned facts; it rearranges with simultaneous separation from metal surface or is reduced without rearrangement



Clemmensen reduction is often accompanied by pinacol formation. Kinetic study (part III) has shown that this reaction is a different reaction from Clemmensen reduction in its mechanism; no intermediate common to both exists. It follows that one-electron reduction is not involved in the first step of the Clemmensen reduction; the first step of this reaction must involve two-electron reduction by which the carbonyl compound is reduced to carbonium ion. This requirement is met by the mechanism described above; that is, zinc forms a complex with the carbonyl compound and goes into solution as a bivalent cation, leaving two electrons on the molecule of carbonyl compound. Pinacol is formed, even in the absence of zinc, by electrochemical reduction at the mercury surface. So the mechanism of pinacol formation accompanying Clemmensen reduction is explained satisfactorily in terms of the electrochemical double electrode theory which states that the dissolution of metal consists of cathodic and anodic reaction occurring simultaneously at different parts of the metal surface[15]

$$\mathrm{Ox} + n\mathrm{H}^+ + ne^- \longrightarrow \mathrm{OxH}_n \qquad \text{cathodic reaction}$$

$$\mathrm{M} - ze^- \longrightarrow \mathrm{M}^{z+} \qquad \text{anodic reaction}$$

$$z\mathrm{Ox} + nz\mathrm{H}^+ + n\mathrm{M} \longrightarrow z\mathrm{OxH}_n + n\mathrm{M}^{z+} \qquad \text{net reaction}$$

where M signifies the metal, Ox the reducible substance and OxH_n the product of reduction. This theory satisfactorily accounts for the mechanism of pinacol formation

$$2\mathrm{RR'CO} + 2e^- + 2\mathrm{H_3O}^+ \longrightarrow \mathrm{RR'COHCOHRR'} + 2\mathrm{H_2O} \qquad \text{cathodic reaction}$$

$$\mathrm{Zn} - 2e^- \longrightarrow \mathrm{Zn}^{2+} \qquad \text{anodic reaction}$$

$$2\mathrm{RR'CO} + \mathrm{Zn} + 2\mathrm{H_3O}^+ \longrightarrow \mathrm{RR'COHCOHRR'} + \mathrm{Zn}^{2+} + 2\mathrm{H_2O} \qquad \text{net reaction}$$

But this theory does not apply to Clemmensen reduction because it is difficult to explain in terms of this theory why two-electron reduction occurs with exclusion of one-electron reduction at the first step of the reaction. A sharp mechanistic distinction should thus be made between these two reactions.

The author's hypothesis differs from that of Brewster[4b] in the following aspect. The latter

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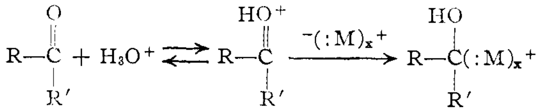
[14] J. O'M. Bockris and A. M. Azzam, *Trans. Faraday Soc.*, **48**, 145 (1952).

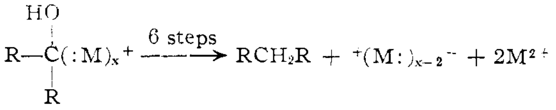
[15] M. G. Fouad and J. F. Herringshaw, *J. Chem. Soc.*, 1207 (1954).

assumes the bond formation between carbon and *massive* metal



$$R-\overset{\overset{O}{\|}}{\underset{R'}{\underset{|}{C}}} + H_3O^+ \rightleftarrows R-\overset{\overset{HO^+}{\|}}{\underset{R'}{\underset{|}{C}}} \xrightarrow{^-(:M)_x{}^+} R-\overset{\overset{HO}{|}}{\underset{R'}{\underset{|}{C}}}(:M)_x{}^+$$

Electrons are transferred to carbon through this bond with dissolution of metal ion from the *massive* metal into the solution



$$R-\overset{\overset{HO}{|}}{\underset{R}{\underset{|}{C}}}(:M)_x{}^+ \xrightarrow{\text{6 steps}} RCH_2R + {}^+(M:)_{x-2}{}^- + 2M^{2+}$$

This mechanism has many features in common with the concept of the free-electron model of the metal and hence with the electrochemical mechanism of the reduction. As explained above, this theory cannot readily account for the fact that the first step of Clemmensen reduction involves two-electron reduction with exclusion of one-electron reduction. The author's hypothesis involves the reaction of carbonyl compound with *zinc atom* as the essential step of Clemmensen reduction: this theory accounts for the fact that electrons are transferred *in pairs* from metal to carbonyl compound

$$RR'CO \xrightarrow{2e^-} \text{carbonium ion} \xrightarrow{2e^-} RCH_2R'$$

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, FACULTY OF LIBERAL ARTS AND EDUCATION, MIYAZAKI UNIVERSITY, MIYAZAKI CITY, MIYAZAKI, JAPAN]

Studies on the Mechanism of Clemmensen Reduction. II. Evidence for the Formation of an Intermediate Carbonium Ion

BY TADAAKI NAKABAYASHI*

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The initial stages of Clemmensen reductions of acetophenone and *t*-butyl phenyl ketone were studied at 60°. The saturated and the unsaturated (and, in the case of *t*-butyl phenyl ketone, rearranged) hydrocarbons are formed from these ketones directly, not by way of the corresponding alcohols. This result suggests that a carbonium ion is the intermediate in Clemmensen reduction.

It has often been stated that in Clemmensen reduction the carbonyl compound is reduced to hydrocarbon by way of the corresponding alcohol. Steinkopf and Wolfram[1] found benzyl alcohol in the reduction product of benzaldehyde and regarded this alcohol as an intermediate of the reduction. They also detected styrene, di-, tri- and polystyrene in the reduction product of acetophenone and considered them to be products of dehydration of the intermediate 1-phenylethanol. Phenylglyoxalic acid gives mandelic acid instead of phenylacetic acid. Martin[2] showed that benzyl alcohol and benzyl chloride give toluene under "Clemmensen's conditions" and concluded that the alcohol and the chloride are intermediates in this reaction. Recently Brewster and co-workers[3] stated that alcohol is an important intermediate in the reduction of aromatic carbonyl compound or sterically hindered ketone but is not in the reduction of aliphatic compounds.

These authors, however, did not prove the intermediacy of alcohol kinetically and, in some cases, did not even prove the formation of the alcohol in the course of Clemmensen reduction. Sometimes the formation of unsaturated product was regarded as evidence for the formation of alcohol. To ascertain the nature of the intermediates of this reaction the author studied the early stages of the reductions of some aromatic ketones under mild conditions avoiding any secondary changes of the reaction products.

Experimental

Materials.—Acetophenone of reagent grade was rectified under reduced pressure and the distillate was purified by crystallization; m.p. 18.5–19.5°. It was distilled just before use. 1-Phenylethanol was prepared by Meerwein-Ponndorf reduction of acetophenone; b.p. 102–103° (20 mm.). *t*-Butyl phenyl ketone was prepared from *t*-butylmagnesium chloride and benzonitrile[4]; b.p. 66–68° (2 mm.). *t*-Butylphenylcarbinol was prepared from *t*-butylmagnesium chloride and benzaldehyde[5]; b.p. 74–75° (2 mm.). The phenylurethan of this alcohol was prepared in the following way. *t*-Butylphenylcarbinol was mixed with an equal volume of phenyl isocyanate and kept for 3 days at room temperature. The unreacted substances were removed by heating the product at 100° under 2 mm. pressure. The residual matter was dissolved in benzene, filtered, petroleum benzine was added to the filtrate, the precipitated crystals were collected, dissolved in benzene and precipitated with petroleum benzine. This process was repeated three times. The white crystals obtained in this way melted at 105.0–105.8°. 2-Methyl-3-phenyl-2-butene was prepared by dehydration of *t*-butylphenylcarbinol with sodium hydrogen sulfate; b.p. 73° (11mm.). Its infrared absorption spectrum[6] had peaks 7.26, 8.28, 8.83, 9.33, 9.74, 10.99, 11.21, 13.07, 14.22μ. These peaks agreed with those reported by Brewster[3] except that at 11.21μ. An additional peak at 7.75μ was reported by him. Neopentylbenzene was prepared from benzylmagnesium chloride and *t*-butyl bromide[7]; b.p. 82° (30mm.). Its infrared absorption spectrum had the following important peaks which agreed with those reported by Brewster[3]: 7.20, 7.31, 8.06, 8.31, 8.72, 9.27, 9.69, 11.14, 12.98, 13.93, 14.22μ. Hydrochloric acid of G.

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(1) W. Steinkopf and A. Wolfram, *Ann.*, **430**, 113 (1923).

(2) E. L. Martin, THIS JOURNAL, **58**, 1438 (1936).

(3) J. H. Brewster and others, *ibid.*, **76**, 6368 (1954).

(4) A. Willemart, *Bull. soc. chim.*, [5] **2**, 867 (1935).

(5) G. Tsatsas, *Ann. chim.*, **1**, 342 (1946).

(6) The infrared spectra were recorded by A. Matsuda of Kyushu University with a Perkin-Elmer 112 infrared spectrophotometer.

(7) A. Bygden, *Ber.*, **45**, 479 (1912).