[CONTRIBUTION NO. 1026 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Kinetics of the Reaction of Dicobalt Octacarbonyl with Hexyne-1 and Hexyne-2[1]

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The rate of reaction of dicobalt octacarbonyl, $Co_2(CO)_8$, with hexyne-1 and with hexyne-2 was investigated. A mathematical analysis of the data is presented and a reaction mechanism is proposed to explain the results. There is kinetic evidence that in solution the stable form of dicobalt octacarbonyl is in equilibrium with a less stable form which is the reactive species. This reactive form may be one in which the cobalt–cobalt bond has been homolytically cleaved. There is also kinetic evidence for an acetylenic dicobalt heptacarbonyl intermediate.

It has been reported[4] recently that dicobalt octacarbonyl reacts with acetylenic compounds producing acetylenic dicobalt hexacarbonyls and evolving carbon monoxide according to the reaction

$$RC{\equiv}CR' + Co_2(CO)_8 \longrightarrow RC_2R'Co_2(CO)_6 + 2CO \quad (1)$$

The purpose of the present paper is to describe a kinetic study in which the rates of reaction of dicobalt octacarbonyl with hexyne-1 and hexyne-2 were determined by measuring the rate of evolution of carbon monoxide. A mathematical analysis of the data is presented and a reaction mechanism is proposed to explain the results.

Experimental

The hexynes and solvents were dried with calcium chloride and/or anhydrous magnesium sulfate and re-distilled: hexyne-1, b.p. 70.5°, $n^{24}D$ 1.3970; hexyne-2, b.p. 82–83°, $n^{24}D$ 1.4127; toluene, b.p. 108–109°; *n*-heptane, b.p. 97–98°.

Dicobalt octacarbonyl was obtained[5] as a solution in a low boiling petroleum ether. In order to change the solvent, the petroleum ether was removed by passing a stream of carbon monoxide over the solution. This procedure was designed to reduce to a minimum the decomposition of the dicobalt octacarbonyl to tetracobalt dodecarbonyl and carbon monoxide. The solid dicobalt octacarbonyl was then weighed and the solvent was added. This new solution of dicobalt octacarbonyl was standardized by measuring the total amount of carbon monoxide evolved from aliquots when an excess of hexyne-1 was added.

The apparatus used for measuring the rate of reaction consisted of a 100- or 200-ml. reaction flask which was equipped with a rubber serum cap for the introduction of the reactants. The flask was immersed in a small water-bath, and the contents of both the bath and the reaction flask were stirred magnetically. In this way the temperature of the reactants was controlled within ±0.5°.

Each reactant was measured and injected into the reaction vessel by means of a hypodermic syringe. The standardized dicobalt octacarbonyl solution and the appropriate amount of additional solvent were introduced into the reaction flask. This solution was saturated with carbon monoxide and then the hexyne was added. The carbon monoxide evolved was passed through a 0° cold trap and then measured at atmospheric pressure and room temperature by displacement of mercury contained in 100-ml. burets.

The initial concentrations *a* and *b* of the dicobalt octacarbonyl and hexyne, respectively, used in the various experiments are shown in Figs. 1 to 6. Unless otherwise indicated the temperature was 25° and the solvent was toluene.

Analysis of the Kinetic Data

The symbols used in this section have the following meanings

A_0 = dicobalt octacarbonyl
B_0 = a reactive form of dicobalt octacarbonyl
X = acetylenic compound
C_0 = acetylenic dicobalt octacarbonyl complex
A_1 = acetylenic dicobalt heptacarbonyl
A_2 = acetylenic dicobalt hexacarbonyl
P = carbon monoxide
a = init. concentration of dicobalt octacarbonyl
b = init. concentration of hexyne

Among the possible mechanisms for reaction 1, one would first consider those of the type

$$A_0 + X \xrightarrow{k_1} A_2 + 2P \qquad \text{(I)}$$

$$A_0 + X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A_2 + 2P \qquad \text{(II)}$$

$$\left.\begin{array}{l} A_0 + X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A_1 + P \\ A_1 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} A_2 + P \end{array}\right\} \qquad \text{(III)}$$

$$A_0 + X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_0 \xrightarrow{k_2} A_2 + 2P \qquad \text{(IV)}$$

and more complicated mechanisms of this type.

However, it can be seen that any mechanism in which A_0 and X occur only in a step of the form

$$A_0 + X \longrightarrow \text{(intermediate and/or product)}$$

leads to an integrated rate law for the product P, as a function of the time, which is symmetrical in the initial concentrations *a* and *b*. The experimental function P is not symmetrical in *a* and *b* (Figs. 1, 2, 4 and 5), but is instead a slightly stronger function of *a* than of *b*. The above type of mechanism is, therefore, ruled out.

Among the mechanisms that would give the observed asymmetry, those that seem most likely are

$$\left.\begin{array}{l} A_0 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B_0 \\ B_0 + X \xrightarrow{k_2} A_2 + 2P \end{array}\right\} \qquad \text{(V)}$$

Same as V, but second step reversible (VI)

$$\left.\begin{array}{l} A_0 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B_0 \\ B_0 + X \xrightarrow{k_2} A_1 + P \\ A_1 \xrightarrow{k_3} A_2 + P \end{array}\right\} \qquad \text{(VII)}$$

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[1] Abstracted from a portion of the Ph.D. Thesis of M. R. Tirpak, University of Pittsburgh, 1958.

[2] Air Reduction Chemical Co. Fellow, 1955–1956.

[3] Diamond Chemical Company, Painesville, Ohio.

[4] H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby and I. Wender, THIS JOURNAL, **78**, 120 (1956).

[5] Courtesy of the Bureau of Mines, Bruceton, Pa.

Same as VII, but second and/or third step reversible (VIII)

$$\begin{aligned} &A_0 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B_0 \\ &B_0 + X \xrightarrow{k_2} C_0 \xrightarrow{k_3} A_2 + 2P \end{aligned} \tag{IX}$$

Same as IX, but second and/or third step reversible (X)

$$\begin{aligned} &A_0 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B_0 \\ &B_0 + X \xrightarrow{k_2} C_0 \xrightarrow{k_3} A_1 + P \\ &A_1 \xrightarrow{k_4} A_2 + P \end{aligned} \tag{XI}$$

Same as XI, but more of the steps reversible. (XII)

In these mechanisms it is assumed that before the addition of the acetylenic compound an equilibrium exists between A_0 and B_0.

In order to treat these mechanisms mathematically it was necessary to assume that either steady state or equilibrium conditions exist for B_0 during the reaction. However, only the steady state assumption gives the aforementioned asymmetry in the product P.

It was not possible with the steady state approximation, or with combinations of the steady state and equilibrium approximations, to fit all of the experimental data with mechanism V, VI, IX, or X. However, a satisfactory fit of all the experimental data was obtained by using mechanism VII with the steady state approximation. Of course, some mechanisms more complicated than VII would also provide satisfactory agreement with the experimental data. For example, any data that are consistent with VII are also consistent with VIII, XI and XII. Since the present purpose was to find the simplest mechanism that accounts for all of the observed results, no mechanisms more complicated than VII were treated numerically.

A mathematical treatment of mechanism VII is given in a following section. The agreement between the theoretical and the experimental results is discussed in the following two sections.

Hexyne-1.—The experimental points for the reaction with hexyne-1 and the theoretical curves are shown in Figs. 1, 2 and 3. The theoretical curves were calculated assuming mechanism VII using the steady state approximation for B_0. These curves correspond to the following values of the rate constants: $k_1 = 1.1 \times 10^{-2}$ sec.$^{-1}$, $(k_{-1} + k_1)/k_2 = 3.6 \times 10^2$ moles liter^{-1}, $k_3 = 8 \times 10^{-3}$ sec.$^{-1}$. However, there is some latitude in the choice of a set of rate constants. For example the set $k_1 = 1.1 \times 10^{-2}$ sec.$^{-1}$, $(k_{-1} + k_1)/k_2 = 3.4 \times 10^2$ moles liter^{-1}, $k_3 = 7 \times 10^{-3}$ sec.$^{-1}$, gives theoretical curves which are not significantly different from those given in Figs. 1, 2 and 3. A reliable estimate of the magnitude of the region over which the constants can vary in a concerted manner has not been obtained. Of primary interest is the fact that a set of values can be found that give satisfactory agreement between the experimental data and mechanism VII.

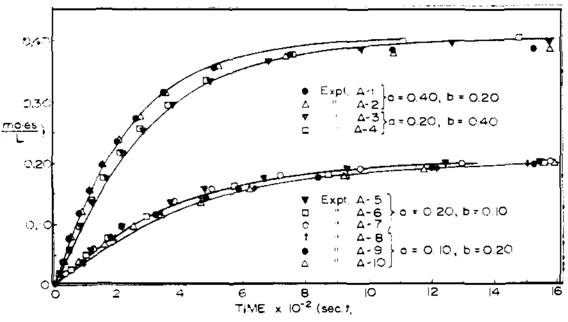


Fig. 1.—Theoretical curves and experimental points for the reaction of hexyne-1 and for the initial concentrations a and b (moles/liter) as indicated.

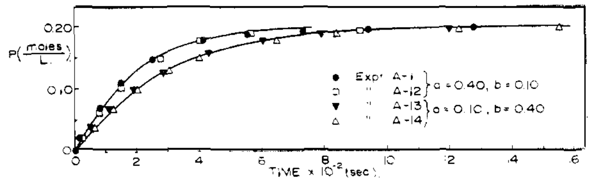


Fig. 2.—Theoretical curves and experimental points for the reaction of hexyne-1 and for the initial concentrations a and b (moles/liter) as indicated.

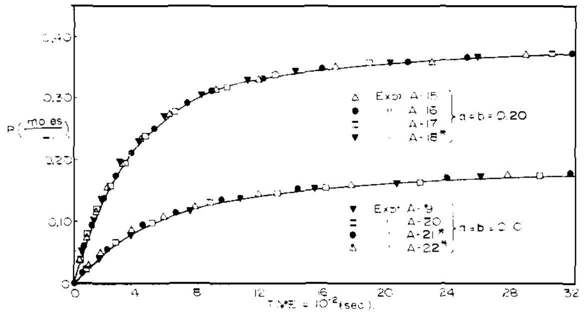


Fig. 3.—Theoretical curves and experimental points for the reaction of hexyne-1 and for the initial concentrations a and b (moles/liter) as indicated. In the experiments marked with the asterisk the reaction took place in the presence of an excess of the product, hexyne-1 dicobalt hexacarbonyl (a moles/liter).

From an experiment carried out at 1° (not shown in the figures) and the experiments which were performed at 25° it is possible to calculate an apparent activation energy E_a for the over-all reaction according to the definition

$$E_a = \frac{RT_1T_2}{(T_2 - T_1)} \ln \frac{t_{1/2}(T_1)}{t_{1/2}(T_2)}$$

where $t_{1/2}(T)$ is the half-life of the reaction at temperature T. From the experiments at 25°, $t_{1/2}$ (298) = 300 sec.; from an experiment at 1°, $t_{1/2}$ (274) = 8400 sec. Therefore, E_a = 23 kcal. mole^{-1}. This would be approximately the activation energy of the rate-determining step which, according to mechanism VII with steady state conditions for B_0, would be the activation energy in k_1.

In one experiment n-heptane was used as the solvent with $a = b = 0.20$ mole liter^{-1}. The rate of reaction in n-heptane was the same, within experimental error (±5%), as the rate in toluene over the entire range of the reaction.

Hexyne-2.—The experimental points and the theoretical curves for the reaction with hexyne-2 are shown in Figs. 4, 5 and 6. As for the case of hexyne-1, these theoretical curves were calculated assuming mechanism VII and using the steady state approximation for B_0. These curves correspond to the following values of the rate constants: $k_1 = 1.1 \times 10^{-2}$ sec.$^{-1}$, $(k_{-1} + k_1)/k_2 = 5.4 \times 10^2$ moles liter^{-1}, $k_3 = 5 \times 10^{-3}$ sec.$^{-1}$. Again, as in the case of hexyne-1, satisfactory agreement between experiment and theory can be obtained by using other combinations of values for the rate constants in the vicinity of those given above. The value of k_1 is the same for the reactions with hexyne-1 and with hexyne-2. This is in agreement with mechanism VII.

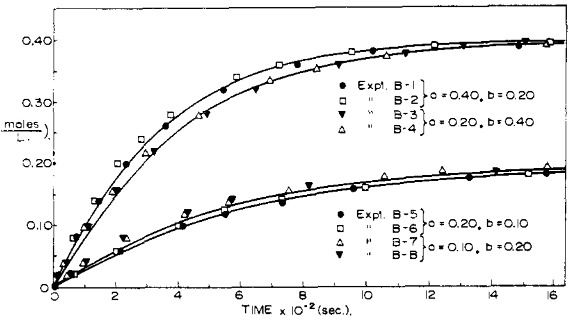


Fig. 4.—Theoretical curves and experimental points for the reaction of hexyne-2 and for the initial concentrations a and b (moles/liter) as indicated.

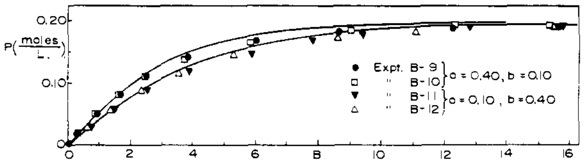
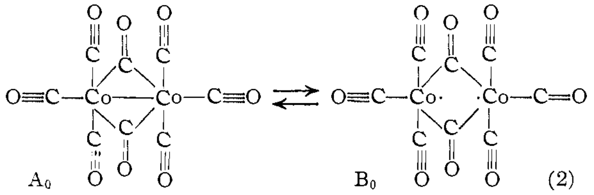


Fig. 5.—Theoretical curves and experimental points for the reaction of hexyne-2 and for the initial concentrations a and b (moles/liter) as indicated.

Discussion.—One possible interpretation of mechanism VII can be described in the following manner: In the accepted structure for dicobalt octacarbonyl[6] there are two bridge carbonyl groups and a cobalt–cobalt bond. In solution, dicobalt octacarbonyl might exist in equilibrium with a less stable form B_0, in which the cobalt–cobalt is homolytically cleaved. That is


A_0 B_0 (2)

The less stable form B_0 would exist in much lower concentration than A_0 in this equilibrium. When the acetylenic compound is added, the reactive form B_0 would quickly reach a steady state concentration. The activation energy, 23 kcal. mole^{-1}, mentioned in a previous section would be approximately the activation energy of the forward step in reactions (2). This would be essentially the difference in the energy of B_0 and A_0, because the activation energy for the formation of the Co–Co bond would be small.

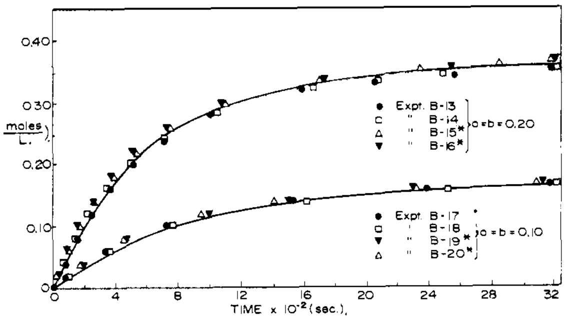
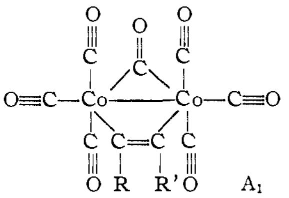


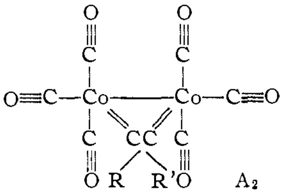
Fig. 6.—Theoretical curves and experimental points for the reaction of hexyne-2 and for the initial concentrations a and b (moles/liter) as indicated. In the experiments marked with the asterisk the reaction took place in the presence of an excess of the product, hexyne-2 dicobalt hexacarbonyl (a moles/liter).

The intermediate A_1 would be an acetylenic dicobalt heptacarbonyl, which might have the structure

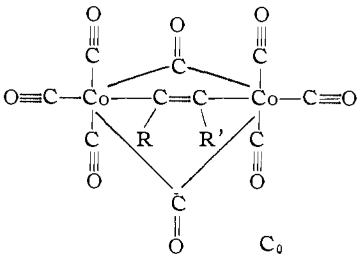

A_1

The intermediate A_1 is similar to the olefin dicobalt heptacarbonyl which has been postulated[7] as an intermediate in the hydroformylation (oxo) reaction.

The final step of the reaction would be the decomposition of A_1 to give the stable product A_2.


A_2

As mentioned earlier, it is not possible by means of the present investigation to distinguish between mechanism VII and a mechanism of the type XI. It is therefore possible that another intermediate C_0 exists with the possible structure


C_0

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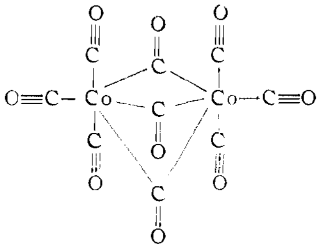
(6) R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, THIS JOURNAL, **77**, 3951 (1955).

(7) I. Wender, S. Metlin, S. Ergun, H. W. Sternberg and H. Greenfield, *ibid.*, **78**, 5401 (1956).

Under certain conditions, a dicobalt nonacarbonyl can be prepared.[8] Its structure may be similar to that proposed for C_0.



Kinetic Derivation

The differential equations for mechanism VII have not been solved exactly. They can, however, be solved by assuming either equilibrium or steady state conditions for B_0.

Equilibrium Approximation.—If A_0 and B_0 remain in equilibrium during the reaction then

$$(B_0) = (k_1/k_{-1})(A_0) \qquad (1)$$

where (A_0) and (B_0) signify the concentrations of A_0 and B_0. Let y represent the amount of B_0 or X, that has reacted; that is, let

$$y = (A_1) + (A_2) \qquad (2)$$

Also

$$a = (A_0) + (B_0) + y \qquad (3)$$

and

$$(X) = (b - y) \qquad (4)$$

where a and b are the initial concentrations of the dicobalt octacarbonyl and the acetylenic compound, respectively. It follows that

$$(B_0) = \frac{k_1(a - y)}{k_{-1} + k_1} \qquad (5)$$

From

$$\mathrm{d}y/\mathrm{d}t = k_2(B_0)\,(X) \qquad (6)$$

one has

$$\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{k_1k_2(a - y)(b - y)}{(k_{-1} + k_1)} \qquad (7)$$

and

$$\frac{\mathrm{d}(A_1)}{\mathrm{d}t} = \frac{\mathrm{d}y}{\mathrm{d}t} - k_3(A_1) \qquad (8)$$

Equation 8 is a linear differential equation with constant coefficients. Its solution can be written as the sum of the complementary function of eq. 8 and a particular integral of eq. 8

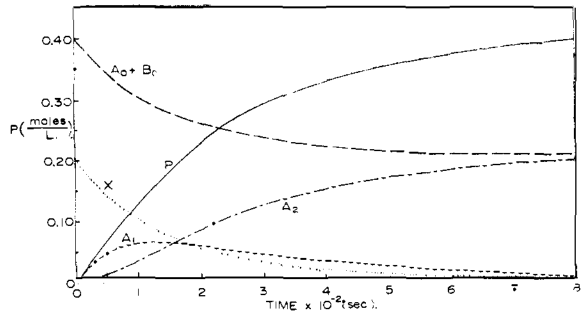


Fig. 7.—Typical theoretical curvesshowing the concentrations of the various chemical species in the reaction of hexyne-1. The initial concentrations (mole/liter) are: a = 0.40 and b = 0.20. Steady-state conditions require that the concentration of B_0 be very low.

$$(A_1) = c_1e^{-k_3t} + e^{-k_3t}\int e^{k_3t}\left(\frac{\mathrm{d}y}{\mathrm{d}t}\right)\mathrm{d}t \qquad (9)$$

where c_1 is a constant. From the fact that $(A_1) = 0$ when $t = 0$, it follows that $c_1 = 0$. Also, since

$$\int e^{k_3t}\left(\frac{\mathrm{d}y}{\mathrm{d}t}\right)\mathrm{d}t = \int e^{k_3t}\,\mathrm{d}y \qquad (10)$$

and since $y = 0$ when $t = 0$, eq. 9 can be written

$$(A_1) = e^{-k_3t}\int_0^y e^{k_3t}\,\mathrm{d}y \qquad (11)$$

Integration of eq. 7 gives, for $a \neq b$

$$t = \left(\frac{k_{-1} + k_1}{k_1k_2}\right)\left(\frac{1}{a - b}\right)\ln\frac{b(a - y)}{a(b - y)} \qquad (12)$$

and, for $a = b$

$$t = \left(\frac{k_{-1} + k_1}{k_1k_2}\right)\left(\frac{y}{a(a - y)}\right) \qquad (13)$$

Since

$$(P) = 2y - (A_1) \qquad (14)$$

it follows that (P) is symmetrical in a and b.

Steady State Approximation.—When steady state conditions exist for B_0, then

$$(B_0) = \frac{k_1(A_0)}{k_{-1} + k_2(X)} \qquad (15)$$

and from eq. 3

$$(A_0) = \left(\frac{k_{-1} + k_2(X)}{k_{-1} + k_2(X) + k_1}\right)(a - y) \qquad (16)$$

It follows from eq. 6 that

$$\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{k_1k_2(a - y)(b - y)}{k_{-1} + k_1 + k_2\,(b - y)} \qquad (17)$$

Integration of eq. 17 gives, for $a \neq$ b

$$t = \left(\frac{k_{-1} + k_1}{k_1k_2}\right)\left(\frac{1}{a - b}\right)\ln\frac{b(a - y)}{a(b - y)} + \frac{1}{k_1}\ln\frac{a}{a - y} \qquad (18)$$

and, for $a = b$

$$t = \left(\frac{k_{-1} + k_1}{k_1k_2}\right)\left(\frac{y}{a(a - y)}\right) + \frac{1}{k_1}\ln\frac{a}{a - y} \qquad (19)$$

The value of (A_1) is again given by eq. 11, and (P) is given by eq. 14. The second term on the right in eqs. 18 and 19 accounts for the asymmetry in a and b of the function (P). Except for this asymmetric term the steady state eqs. 18 and 19 are the same as the equilibrium eqs. 12 and 13, respectively.

Numerical Treatment.—The following procedure was used to fit the theoretical curves for (P) to the experimental data:

With estimated values for $(k_{-1} + k_1)/k_1k_2$, k_1 and k_3, in equation 18 or 19, t was calculated as a function of y. From this function a graph of e^{k_3t} as a function of y was obtained, and the graph was used with eq. 11 to obtain (A_1) by graphical integration. Equation 14 was then used to calculate (P) as a function of t. The theoretical curve was compared with the experimental curve to obtain better estimates of the constants $(k_{-1} + k_1)/k_1k_2$, k_1 and k_3. This process was repeated

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[8] H. W. Sternberg, R. Markby and I. Wender, unpublished work at the Bureau of Mines, Bruceton, Pa.

until a satisfactory agreement between the theoretical and experimental curves was obtained. The procedure was essentially one of trial and error combined with semi-quantitative predictions of the effects of changes in the values of the constants.

In Fig. 7 are shown typical theoretical curves for $(A_0) + (B_0)$, (A_1), (A_2), (X) and (P). These curves are for the reaction of hexyne-1 with $a = 0.40$ mole liter^{-1}, $b = 0.20$ mole liter^{-1}, and with the following values of the rate constants: $k_1 = 1.1 \times 10^{-2}$ sec.$^{-1}$, $(k_{-1} + k_1)/k_2 = 3.6 \times 10^2$ moles liter^{-1}, $k_3 = 8 \times 10^{-3}$ sec.$^{-1}$.

Acknowledgment.—The authors wish to thank Dr. H. W. Sternberg and Dr. I. Wender, Bureau of Mines, Bruceton, Pa., for helpful discussions during this investigation. They also wish to thank Sol Metlin, Bureau of Mines, Bruceton, Pa., for preparing the dicobalt octacarbonyl that was used in this study.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Diaryliodonium Salts. V. The Electroreduction of Diphenyliodonium Salts[1,2]

BY H. ELIZABETH BACHOFNER, F. MARSHALL BERINGER AND LOUIS MEITES

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The electroreduction of diphenyliodonium salts has been investigated both by polarography at the dropping mercury electrode and by coulometry at controlled potential. The three polarographic waves are shown to correspond to the processes: (I) $R\overset{+}{I}R + e \rightleftarrows R\dot{I}R$; (II) $R\overset{+}{I}R + 2e + H^+ \rightarrow RH + RI$; (III) $R\overset{+}{I}R + 4e + H^+ \rightarrow RH + R^- + I^-$ (slow); $R^- + H^+ \rightarrow RH$ (fast). Diphenyliodine produced by controlled-potential electrolysis is unstable and decomposes rapidly to iodobenzene and other products. Those variables whose effects on the polarographic reduction have been investigated include the nature of the anion, the composition of the solvent, the concentration of the diphenyliodonium ion, the ionic strength and the *p*H and nature of the buffer system. A paper on the effects of substituents follows directly.

Introduction

The preceding papers in this series of publications on iodonium salts include discussions of the synthesis[3] and reactions[2,4,5] of these compounds; the present paper will discuss their electrochemical reduction at both small and large mercury electrodes.

The only previously reported work[6] on the polarography of iodonium salts was restricted to unsubstituted diphenyliodonium salts and to phenyl-β-chlorovinyliodonium salts. For both groups of salts the authors reported polarograms with four waves and postulated a stepwise reduction involving a total of four electrons. Reduction *via* the phenylmercury free radical was postulated in analogy with the reduction of a phenylmercuric salt.[7] Wawzonek, however, in his recent review article[8a] has reinterpreted Colichman's data and has proposed another mechanism, also involving phenylmercury intermediates. The question of organomercury compounds as possible intermediates in the electroreduction of iodonium salts will be considered later.

A large-scale electrolysis of diaryliodonium hydroxide at 4.5 volts led to products which indicated to the investigators that aryl radicals were reduction products.[9]

Included among the various other 'onium salts for which the polarographic or electrolytic reduction has been investigated are quaternary ammonium,[10a] N-alkylpyridinium,[10b] tetrazolium,[10c] benzenediazonium,[10d] triphenylsulfonium,[10e] tetraarylphosphonium[10f] and aryltrialkylphosphonium[10f] salts.

The polarography of aliphatic and aromatic halides is discussed by Kolthoff and Lingane[11] and has been brought up to date in the review articles by Wawzonek.[8] In the majority of cases the halide is reduced to the hydrocarbon. This mechanism has been confirmed coulometrically.[12]

$$RX + 2e^- + H^+ \longrightarrow RH + X^-$$

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[1] This paper is based on a dissertation submitted by Miss Hilde Elizabeth Bachofner in partial fulfillment of the requirements of the degree of Doctor of Philosophy in 1957 and was presented in part at the 130th National Meeting of the American Chemical Society at Atlantic City in September, 1956 (Abstracts of Papers, p. 85-O).

[2] Previous paper: F. M. Beringer, E. J. Geering, M. Mausner and I. Kuntz, *J. Phys. Chem.*, **60**, 141 (1956).

[3] F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953).

[4] F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *ibid.*, **75**, 2708 (1953).

[5] F. M. Beringer and E. M. Gindler, *ibid.*, **77**, 3200, 3203 (1955).

[6] (a) E. L. Colichman and H. P. Maffei, *ibid.*, **74**, 2744 (1952); (b) E. L. Colichman and J. T. Matschiner, *J. Org. Chem.*, **18**, 1124; (1953).

[7] R. Benesch and R. E. Benesch, THIS JOURNAL, **73**, 3391 (1951). These workers reported the separate addition of two electrons, the first to form the phenylmercury free radical, the second, with addition of a proton, to form benzene and metallic mercury. Colichman and Maffei (ref. 6a) found the half-wave potential for their wave III of diphenyliodonium iodide to be −0.87 to −1.22 *vs.* S.C.E., depending on *p*H while Benesch and Benesch had found that the phenylmercuric salt took up the second electron at −0.8 to −1.2 v., depending on *p*H and concentration.

[8] (a) S. Wawzonek, *Anal. Chem.*, **26**, 65 (1954); (b) **24**, 32 (1952); (c) **28**, 638 (1956).

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