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Polarography of Halides in Dimethylformamide. VI. The Formation of the Benzhydryl Radical from Benzhydryl Bromide and Its Subsequent Reduction at the Dropping Mercury Electrode

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The polarographic behavior of benzhydryl bromide at the dropping mercury electrode was investigated in dimethylformamide at 25°C. It gives three waves, with half-wave potentials at about $+0.19$, -0.15, and -1.00 V *vs.* SCE. The first wave is anodic, while the others are cathodic. It was concluded that benzhydryl bromide, prior to being electrolytically reduced, rapidly reacts with the mercury of the cathode according to the following equation:

$$3(C_6H_5)_2CHBr + Hg \longrightarrow 2(C_6H_5)_2CH\cdot + (C_6H_5)_2CH^+ + HgBr_3^-$$

The first wave given by the bromide was ascribed to the oxidation of $HgBr_3^-$ to $HgBr_2$; the second, to the reduction of $HgBr_3^-$ to Hg and Br^-, and the third, to the reduction of $(C_6H_5)_2CH\cdot$ to $(C_6H_5)_2CH^-$. The cation, $(C_6H_5)_2CH^+$, was found to give no wave. Such behavior of benzhydryl bromide was discussed in comparison with that of the corresponding chloride, which gives a single wave with a usual two-electron transfer.

Organic halides are not always electrolyzed in a usual two-electron reduction, followed by the uptake of the hydrogen ions to yield the corresponding hydrocarbons. For example, when an organic halide reacts rapidly with the mercury used as the indicator electrode, the electrode process can differ from those of usual halides which are reduced in two-electron steps. Thus, Keller *et al.*[1] have polarographically shown that the mercury may remove two chlorine atoms from 1,1-di-*p*-chlorophenyl-1,2,2,2-tetrachloroethane before the electron transfer occurs and thus form 1,1-di-*p*-chlorophenyl-2,2-dichloroethylene, which in turn is electrolytically reduced. Wawzonek *et al.*[2] have shown that benzyl iodide in acetonitrile, prior to being electrolytically reduced, reacts with the mercury of the indicator electrode to yield benzylmercuric iodide, which is then reduced to toluene, mercury, and the iodide ion. Similar examples can also be seen in benzotrichloride,[3] diphenyldichloromethane,[3] and triphenylmethyl chloride.[4] These indicate that polarography with the dropping mercury electrode is a useful means of elucidating the mechanisms of the reactions between mercury and the organic species which are reactive to mercury.

In the present paper, we will examine the polarographic behavior of benzhydryl bromide in dimethylformamide (DMF). The bromide was found to give unusual polarographic waves as a result of its reaction with mercury preceding the electrolytic reduction. The mechanism of the chemical and electrochemical reactions of the bromide at the dropping mercury

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[1] H. Keller, M. Hochweber, and H. von Halban, *Helv. Chim. Acta*, **29**, 761 (1946).

[2] S. Wawzonek, R. C. Duty, and J. H. Wagenknecht, *J. Electrochem. Soc.*, **111**, 74 (1964).

[3] S. Wawzonek and R. C. Duty, *ibid.*, **108**, 1135 (1961).

[4] P. J. Elving and J. M. Markovitz, *J. Phys. Chem.*, **65**, 686 (1961).

electrode will be discussed in detail on the basis of the results of DC polarography and large-scale electrolysis at a controlled potential.

Results and Discussion

Polarographic Behavior of Benzhydryl Bromide. The polarographic behavior of benzhydryl bromide at the dropping mercury electrode was investigated in DMF containing 0.10 M tetraethylammonium perchlorate at 25°C. The bromide gives three waves; the first wave is anodic,[5] while the others are cathodic (Fig. 1). The ratio of the heights of these waves is approximately 1 : 2 : 2. However, the height of the third wave decreases with the time, while those of the first and second waves remain constant (Table 1). The decrease in the height of the third wave can be accelerated by stirring the cell solution, but it is appreciably suppressed by using the platinum foil as the anode instead of the mercury pool. So far as the test solution is allowed to stand without contact with mercury, the height of the third wave does not decrease. These facts indicate that benzhydryl bromide reacts with mercury to form at least two electroactive species, one of which must be labile. Accordingly, the measurement of the polarogram of this depolarizer was always started as soon as possible after the test solution had come into contact with the mercury.

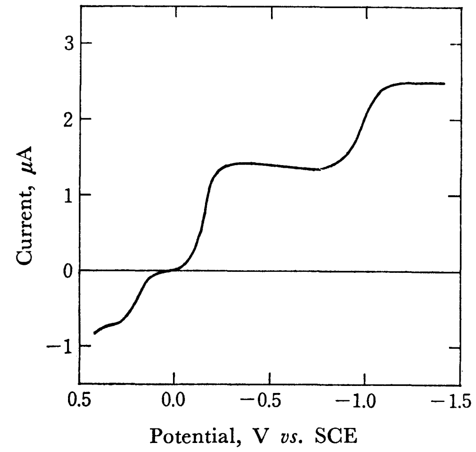

Fig. 1. Polarogram of 0.75 mM $(C_6H_5)_2CHBr$ in DMF containing 0.1 M Et_4NClO_4 at 25°C.

Table 1. Change of the heights of the waves given by benzhydryl bromide[a)] with the time (25°C)

Time[b)] (min)	i_d (μA)		
	1st wave	2nd wave	3rd wave
2	1.20	2.38	2.11
120	1.18	2.39	1.87
180	1.22	2.47	1.30
260	1.17	2.13	1.00

a) 1.0 mM.
b) The time was measured after the addition of mercury to the test solution.

The polarographic characteristics of the bromide at various concentrations are given in Table 2. The height of each wave is practically proportional to the concentration of the depolarizer and to the square root of the height of the mercury reservoir; these facts indicate that each wave is diffusion-controlled. The diffusion coefficient of the bromide, calculated from the Ilkovic equation on the assumption that the third wave is due to a one-electron reduction, is equal to 3.3×10^{-6} cm^2/sec; this value is too small to be regarded as the true value. We will discuss this question again later. It was also found that the half-wave potential of the third wave is practically independent of the concentration of the depolarizer, whereas that of the second wave shifts to the more negative potentials with an increase in the concentration. Because of the considerable irregularity of the plots given, no trends were obtained as to the change in the half-wave potential of the first wave with the concentration.

Table 2. Polarographic characteristics of benzhydryl bromide at various concentrations (25°C)

Concn. (mM)	$E_{1/2}$ (V *vs.* SCE)			I_d[a)]		
	1st wave	2nd wave	3rd wave	1st wave	2nd wave	3rd wave
0.10	+0.171	−0.114	−0.977	0.56	1.32	1.18
0.25	+0.193	−0.120	−0.962	0.56	1.03	0.86
0.50	+0.188	−0.129	−0.967	0.52	1.04	1.07
0.75	+0.210	−0.131	−0.964	0.58	1.08	0.95
1.00	+0.166	−0.153	−1.000	0.56	1.04	1.10
1.50	+0.185	−0.176	−1.009	0.53	0.99	1.11
2.00	+0.212	−0.162	−1.009	0.56	1.08	1.01
2.50	+0.193	−0.195	−1.067	0.61	1.14	1.14

a) $I_d = i_d/Cm^{2/3}t^{1/6}$.

Comparison of the Polarographic Behavior of Benzhydryl Bromide with That of the Corresponding Chloride. The polarogram of benzhydryl chloride is in clear contrast to that of the corresponding bromide. The former gives only a single reduction wave (Fig. 2), although a maximum appears at depolarizer concentrations higher than 0.8 mM. The polarographic characteristics of the chloride at various concentrations are shown in Table 3. The height of the wave is virtually proportional to the concentration of the depolarizer; this indicates that the wave is diffusion-controlled. The diffusion coefficient of the chloride, calculated from the Ilkovic equation on the assumption that the wave is due to a two-electron step, is equal to 11.3×10^{-6} cm^2/sec; this value is fairly appropriate for this molecule. The marked difference in the polaro-

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[5] When the solution of the bromide in DMF was fresh enough, the first wave was cathodic in part; it then turned anodic in time. The change did not stop until the first wave became completely anodic. It seems that this change is closely related to the simultaneously-occurring increase in the specific conductance of the bromide solution, as will be shown in Fig. 5. Thus, it is evident that the bromide undergoes ionization in DMF to form the ion-pair intermediate, and that the polarographic behavior of the resulting ionic species is different from that of the bromide in a covalently-bonded initial state. In the present study, the bromide was always allowed to stand in DMF for at least 3 hr before being used. Accordingly, most of the bromide might have been ionized by the time it was examined.

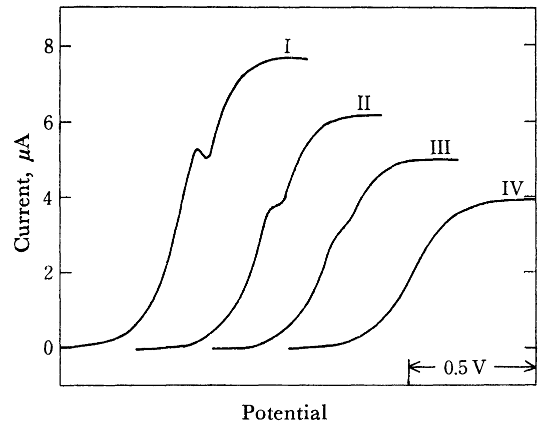

Fig. 2. Polarograms of $(C_6H_5)_2CHCl$ in DMF containing 0.1 M Et_4NClO_4 at 25°C. Each recording was started from −1.20 V *vs.* SCE.
I, 1.2 mM; II, 1.0 mM; III, 0.8 mM; IV, 0.6 mM

Table 3. Polarographic characteristics of benzhydryl chloride at various concentrations (25°C)

Concn. (mM)	$E_{1/2}$ (V *vs.* SCE)	I_d[a)]
0.10	−1.642	5.16
0.30	−1.675	4.07
0.50	−1.664	4.16
0.60	−1.679	4.07
0.80	b)	4.03
1.00	b)	4.07
1.20	b)	4.06
2.00	b)	4.00

a) $I_d=i_d/Cm^{2/3}t^{1/6}$.
b) Impossible to measure owing to the maximum.

graphic behavior between the chloride and the bromide may be related to the difference in their reactivities with mercury. As has been described above, benzhydryl bromide in DMF reacts rapidly with mercury. It seems that the rate of the reaction is determined by the diffusion of the bromide. On the other hand, benzhydryl chloride in DMF reacts very slowly with mercury. When a solution of the chloride in DMF was stirred with mercury at 25°C, the height of the polarographic wave resulting from the reduction of the chloride decreased very slowly with the time (Fig. 3). At the same time, two new waves appeared in the less negative potential region, and they increased with the time. The new waves were closely similar in characteristics to the first and second waves of benzhydryl bromide; the first was anodic, the second was cathodic, and the ratio of the wave heights was about 1 : 2.

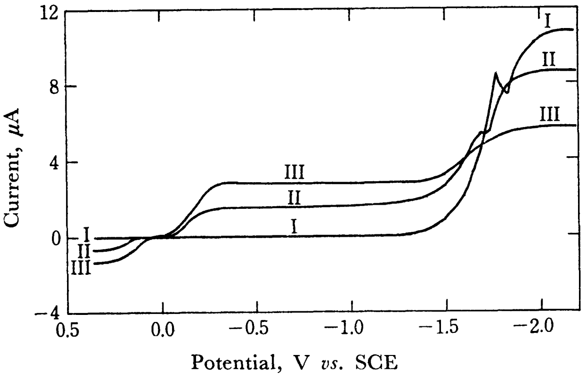

Fig. 3. Change of the polarogram of $(C_6H_5)_2CHCl$ (1.68 mM) in DMF at 25°C with the time.
I, 0 min; II, 2.0 days; III, 10.0 days after the addition of mercury to the test solution

The First and the Second Waves of Benzhydryl Bromide. It was noticed that the first and the second polarographic waves of benzhydryl bromide, as well as those of the reaction mixture of benzhydryl chloride with mercury, are very similar to the waves of the trihalogenomercurate ion. As has been shown in previous papers,[6,7] the trihalogenomercurate ion gives two waves, at about +0.2 and −0.15 V *vs.* SCE; the first is anodic, the second is cathodic, and the ratio between the heights of the waves is approximately equal to 1 : 2. This suggests that benzhydryl bromide and chloride react with mercury to form the tribromo- and trichloromercurate ions respectively. The reaction of benzhydryl bromide with mercury may be so rapid that it precedes the electrolytic reduction. Hence, the bromide gives the waves due to the electrolysis of the tribromomercurate ion instead of those due to the electrolysis of benzhydryl bromide itself.

This conclusion was substantiated by the analysis of the waves given by benzhydryl bromide. The electrode reactions of the tribromomercurate ion at the dropping mercury electrode can be expressed in terms of the following equations:[6]

$$\text{1st wave: } 2\,HgBr_3^- + Hg \rightleftarrows 3\,HgBr_2 + 2\,e \qquad (1)$$

$$\text{2nd wave: } 2\,HgBr_3^- + 4\,e \rightleftarrows 2\,Hg + 6\,Br^- \qquad (2)$$

If the first and the second waves of benzhydryl bromide are due to the depolarization by the tribromomercurate ion, the following relations between current and potential, which have shown to hold for the waves of the latter,[6] should hold for those of the former:

$$\text{1st wave: } E = C_1 + (\boldsymbol{RT}/2\boldsymbol{F})\ln i^3/(i_d-i)^2 \qquad (3)$$

$$\text{2nd wave: } E = C_2 - (\boldsymbol{RT}/2\boldsymbol{F})\ln i^3/(i_d-i) \qquad (4)$$

The results of the analyses of these waves, as well as that of the third wave, are given in Fig. 4. A nearly linear relation was obtained for each of these waves; this means that the presumption presented above is valid. From Eqs. (3) and (4) we can easily derive the relation between the half-wave potential and the concentration of the depolarizer,[6] which shows that the half-wave potential of the first wave should shift to more positive potentials, and that of the second wave, to more negative potentials, with an increase in the depolarizer concentration. The results in Table 2 show that this speculation is also valid, although the data for the first wave show considerable scatter.

The Third Wave of Benzhydryl Bromide. It was found that the height of each of the waves given by 1.0 mM of the tribromomercurate ion (I_d's=1.95 and

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[6] Y. Matsui, R. Kawakado, and Y. Date, This Bulletin, **41**, 2913 (1968).

[7] Y. Matsui, Y. Kurosaki, and Y. Date, *ibid.*, **43**, 2046 (1970).

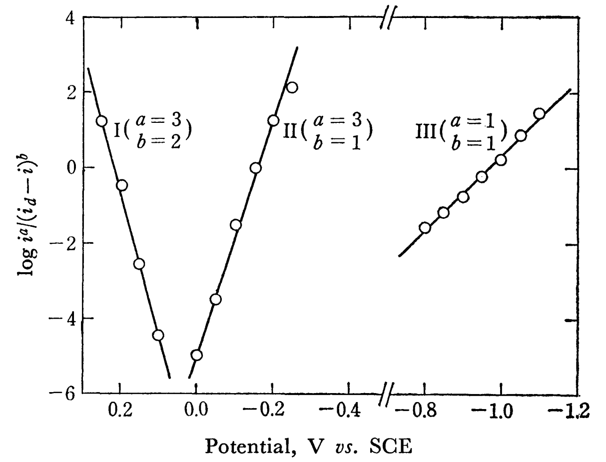

Fig. 4. Analysis of the polarograms of 0.75 mM $(C_6H_5)_2CHBr$ in DMF.
Reciprocal slopes: I, 0.029 V; II, −0.031 V; III, −0.098 V

3.54 for the first and the second waves respectively[6]) is about three times that of the corresponding waves given by 1.0 mM of benzhydryl bromide; this indicates that three moles of benzhydryl bromide react with one gram-atom of mercury to yield one mole of the tribromomercurate ion. Hence, the following stoichiometric equation seems the most probable:

$$3\,(C_6H_5)_2CHBr + Hg \longrightarrow$$
$$2\,(C_6H_5)_2CH\cdot + (C_6H_5)_2CH^+ + HgBr_3^- \qquad (5)$$

Provided that the reaction expressed by Eq. (5) precedes the electrolytic reduction of benzhydryl bromide itself, the third wave of the bromide may be ascribed either to the reduction of the benzhydryl radical or to that of the benzhydryl cation. In order to make this point clear, we examined the polarographic behavior of an equimolar solution of benzhydryl bromide and mercuric bromide in DMF. The reaction between them is fairly rapid, as is shown by the rapid increase in the conductance of the solution (Fig. 5), while the conductance of the DMF solution containing only benzhydryl bromide shows a slower increase with the time. The polarogram of the equimolar solution is shown in Fig. 6. Although the two waves corresponding to the electrolyses of the tribromomercurate ion appeared, no wave arose in the potential region where the third wave of benzhydryl bromide appeared. This shows that benzhydryl bromide reacts with mercuric bromide and yields the tribromomercurate ion, together with the benzhydryl cation; the latter, however, gives no polarographic wave. The cation thus formed may be so labile that it may rapidly react either with the solvent or with the moisture in the solution to form electrolytically-inert species, such as the strongly solvated benzhydryl cation or benzhydrol. Accordingly, the third wave of benzhydryl bromide can be ascribed to the reduction of the benzhydryl radical (Eq. (6)). This is substantiated by the identification of the reaction products, to be described later.

$$\text{3rd wave: } (C_6H_5)_2CH\cdot + e \rightleftarrows (C_6H_5)_2CH^- \qquad (6)$$

It is evident that we can explain, in terms of the chemical reaction expressed by Eq. (5) and the subsequent electrochemical reactions expressed by Eqs. (1), (2), and (6), the fact that the ratio among the three waves of the bromide is approximately 1 : 2 : 2. Moreover, the diffusion coefficient of the bromide calculated on the basis of this mechanism equals 7.4×10^{-6} cm^2/sec; this value seems appropriate for the depolarizer. The decrease in the height of the third wave of benzhydryl bromide with the time can also be explained in terms of the above mechanism. During repeated measurements of the polarograms, benzhydryl bromide reacts with mercury, mainly that of the mercury pool. The resulting benzhydryl radical is so unstable that it dimerizes to form *sym*-tetraphenylethane, which is electrolytically inert. Since the decrease in the concentration of benzhydryl bromide in the cell solution is accompanied by no increase in the concentration of the benzhydryl radical, the height of the third wave decreases with the time. On the other hand, the decrease in the concentration of benzhydryl bromide is accompanied by an increase in the concentration of the tribromomercurate ion. Therefore, the heights of the first and the second waves scarcely change at all with the time.

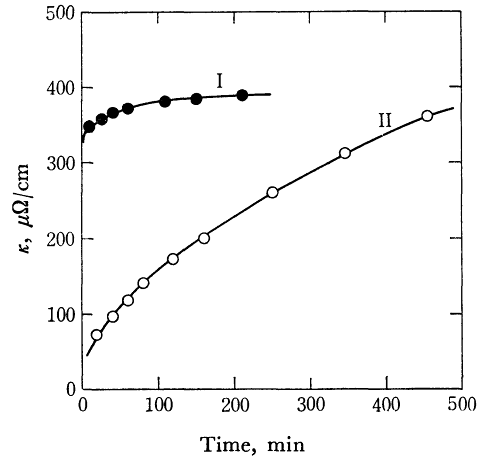

Fig. 5. Plots of the conductance *vs.* the time.
I: $(C_6H_5)_2CHBr$ (44.4 mM) + $HgBr_2$ (44.4 mM) in DMF
II: $(C_6H_5)_2CHBr$ (83.4 mM) in DMF

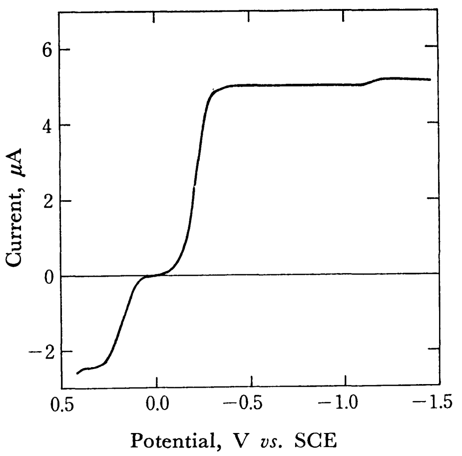

Fig. 6. Polarogram of the equimolar solution (0.83 mM) of $(C_6H_5)_2CHBr$ and $HgBr_2$ in DMF at 25°C.

The logarithmic plot of the third wave is shown in Fig. 4. A nearly linear relation was obtained between the potential and $\log i/(i_d-i)$ with the reciprocal slope of 0.098 V, indicating that the electrode reaction is irreversible.

It is noteworthy that the half-wave potential of the labile benzhydryl radical is less negative by 0.67 V than that of benzhydryl chloride. The polarographic reduction of organic halide is usually expressed in terms of the following reactions:[8]

$$\mathrm{RX} + \mathrm{e} \rightleftarrows \mathrm{R}\cdot + \mathrm{X}^- \tag{7}$$

$$\mathrm{R}\cdot + \mathrm{e} \longrightarrow \mathrm{R}^- \tag{8}$$

$$\mathrm{R}^- + \text{solvent} \longrightarrow \mathrm{RH} \tag{9}$$

Among these reactions, the one expressed by Eq. (7) is considered to be the potential-determining step, for the radical, R·, may be more reducible than the starting halide. Thus, once the halide is electrolytically reduced to the corresponding radical, the latter may immediately be reduced to the corresponding carbanion at the same potential. However, the half-wave potential of such an unstable organic radical had never actually been measured until, in the present experiment, it was shown that the half-wave potential of the benzhydryl radical is less negative than that of the corresponding chloride.

Identification of Reaction Products. Benzhydryl bromide in DMF containing 0.10 M tetraethylammonium perchlorate was reacted with mercury in an atmosphere of nitrogen. From the reaction mixture, *sym*-tetraphenylethane, benzophenone, and benzhydrol were isolated by chromatography in 46, 6, and 34% yields respectively, based on the starting bromide (see the Experimental section). It seems that the *sym*-tetraphenylethane is formed by the dimerization of the benzhydryl radical. It might be considered that the benzophenone is an impurity contained in the starting bromide. However, it is known[9] that the radicals with α-hydrogens, such as the benzhydryl radical, react with oxygen and form the corresponding ketones, together with the corresponding alcohols, according to the following reactions (see also the subsequent paragraph):

$$\mathrm{R_2CH}\cdot + \mathrm{O_2} \longrightarrow \mathrm{R_2CHOO}\cdot \tag{10}$$

$$2\,\mathrm{R_2CHOO}\cdot \longrightarrow \mathrm{R_2CO} + \mathrm{R_2CHOH} + \mathrm{O_2} \tag{11}$$

Thus, it seems that at least a part of the benzophenone, as well as a part of the benzhydrol, may be formed by the reaction of the benzhydryl radical with the small amount of oxygen contained in the nitrogen. The main part of the benzhydrol may be formed by the hydrolysis of the solvated benzhydryl cation. Thus, the reaction products can be classified into two groups, *i.e.*, the products obtained *via* the benzhydryl radical and those obtained *via* the benzhydryl cation; it is evident that the number of the moles of the former is approximately twice that of the latter. Furthermore, it was found that in this reaction *ca.* 1.0 g-atom of mercury is consumed per three moles of the benzhydryl bromide. These results indicate that Eq. (5) is valid.

When benzhydryl bromide was allowed to react with mercury in a stream of dry air, the yield of *sym*-tetraphenylethane based on the starting bromide decreased to 18%, whereas those of benzophenone and benzhydrol increased significantly, to 24 and 45% respectively. Dibenzhydryl ether, which may be produced by the reaction of the benzhydryl cation with benzhydrol, was also obtained in an 8% yield. These results agree well with those to be expected from Eqs. (10) and (11).

In order to examine the effect of the solvent on the present reaction, benzhydryl bromide was allowed to react with mercury in benzene. It was found that *sym*-tetraphenylethane is formed quantitatively, while benzophenone and benzhydrol are scarcely formed at all. It was also found that mercurous bromide is quantitatively formed at the same time. These results indicate that the solvent plays an important role in the present reaction. It is known[6] that the tribromomercurate ion, as well as mercuric bromide, is extremely stable in DMF, while mercurous bromide is insoluble in DMF and decomposes in part to form mercury and mercuric bromide. Hence, benzhydryl bromide in DMF reacts with mercury to yield the most stable species of the brominated mercurys, *i.e.*, the tribromomercurate ion, together with the benzhydryl radical and the benzhydryl cation. On the other hand, in benzene mercurous bromide may be more stable than either mercuric bromide or the tribromomercurate ion. Thus, the benzhydryl bromide in benzene reacts with mercury to form mercurous bromide and the benzhydryl radical, but the benzhydryl cation may not be formed in this case.

When benzhydryl bromide in DMF was electrolyzed with the Hg cathode at the controlled potential of −0.60 V *vs.* SCE, where the limiting current corresponding to the second polarographic wave of the bromide flows, an almost quantitative yield (89%) of *sym*-tetraphenylethane was obtained. The quantity of electricity (n) required for the reduction of one mole of the depolarizer was found to be 1.10 Faradays. These results can be explained in terms of the following mechanism:

$$3\,(\mathrm{C_6H_5})_2\mathrm{CHBr} + \mathrm{Hg} \longrightarrow$$

$$2\,(\mathrm{C_6H_5})_2\mathrm{CH}\cdot + (\mathrm{C_6H_5})_2\mathrm{CH}^+ + \mathrm{HgBr_3}^-$$

$$\mathrm{HgBr_3}^- + 2\,\mathrm{e} \rightleftarrows \mathrm{Hg} + 3\,\mathrm{Br}^-$$

$$(\mathrm{C_6H_5})_2\mathrm{CH}^+ + \mathrm{Br}^- \longrightarrow (\mathrm{C_6H_5})_2\mathrm{CHBr} \tag{12}$$

$$2\,(\mathrm{C_6H_5})_2\mathrm{CH}\cdot \longrightarrow (\mathrm{C_6H_5})_2\mathrm{CHCH}(\mathrm{C_6H_5})_2 \tag{13}$$

The bromide ion, formed by the reduction of the tribromomercurate ion at −0.60 V *vs.* SCE, may react with the solvated benzhydryl cation, thus regenerating the original benzhydryl bromide. Thus, none of the products expected to be formed *via* the benzhydryl cation are obtained. Furthermore, it can also be explained in terms of the above mechanism that the value of n is virtually equal to 1.0 Faraday rather than to the 0.67 Faraday which is to be expected from the results of the DC polarography.

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8) P. J. Elving and B. Pullman, "Advances in Chemical Physics," Vol. III, ed. by I. Prigogine, Interscience Publishers, New York, N. Y. (1961), p. 1.

9) C. Walling, "Free Radicals in Solution," John Wiley & Sons, New York, N. Y. (1957), p. 423.

The electrolytic reduction of benzhydryl bromide with the Hg cathode at the controlled potential of −1.40 V *vs.* SCE, where the limiting current of the third polarographic wave of the bromide flows, resulted in the formation of 38% of diphenylmethane and 51% of *sym*-tetraphenylethane, based on the original bromide. The value of *n* was measured to be 1.13 Faradays. These results can be explained by the following mechanism:

$$3\,(C_6H_5)_2CHBr + Hg \longrightarrow$$

$$2\,(C_6H_5)_2CH\cdot + (C_6H_5)_2CH^+ + HgBr_3{}^-$$

$$HgBr_3{}^- + 2\,e \rightleftarrows Hg + 3\,Br^-$$

$$2\,(C_6H_5)_2CH\cdot + 2\,e \rightleftarrows 2\,(C_6H_5)_2CH^-$$

$$(C_6H_5)_2CH^- + \text{solvent} \longrightarrow (C_6H_5)_2CH_2 \qquad (14)$$

$$(C_6H_5)_2CH^- + (C_6H_5)CH^+ \longrightarrow (C_6H_5)_2CHCH(C_6H_5)_2 \qquad (15)$$

Since diphenylmethane has never been obtained until the present run, it is obvious that the substance is formed *via* the benzhydryl anion. About a half of the benzhydryl anion generated may react with the solvated benzhydryl cation to form *sym*-tetraphenylethane. According to the above mechanism, the value of *n* should equal 1.33 Faradays; this value agrees roughly with that observed.

The electrolytic reduction of benzhydryl chloride at the controlled potential of −2.13 V *vs.* SCE, where the limiting current corresponding to the single polarographic wave of the chloride flows, resulted in the formation of 46% of diphenylmethane and 6% of *sym*-tetraphenylethane. It is remarkable that the yield of diphenylmethane is much higher than that of *sym*-tetraphenylethane, unlike the case of benzhydryl bromide. This indicates that the benzhydryl anion has reacted with the solvent to form diphenylmethane before it reacts with the benzhydryl chloride diffusing toward the electrode to form *sym*-tetraphenylethane. On the other hand, when benzhydryl bromide is the depolarizer, the formation of the benzhydryl cation by the chemical process, together with that of the benzhydryl anion by the electrochemical process, occurs on the electrode surface. Hence, the yield of the product due to the combination of the anion with the cation, *i.e.*, the yield of *sym*-tetraphenylethane, increases significantly.

Experimental

Materials. The DMF used as a solvent was purified as has been described previously.[10] The tetraethylammonium perchlorate used as a supporting electrolyte was prepared according to the directions of Fujinaga *et al.*[11] The benzhydryl bromide was prepared by the reaction of bromine with diphenylmethane[12] (bp 148—150°C/5 mmHg). The benzhydryl chloride was prepared by the reaction of thionyl chloride with benzhydrol[13] (bp 131—133.5°C/7 mmHg). Mercuric bromide obtained commercially was purified by recrystallizing it from ethanol.

Procedure. DC polarography, large-scale electrolysis at a controlled potential, and conductivity measurements were carried out as has been described previously.[6] All the potential measurements were done with reference to an aqueous saturated calomel electrode connected with the cell solution by a DMF-agar salt bridge.[14] The dropping mercury electrode used had the following characteristics in a 0.10 M solution of tetraethylammonium perchlorate in DMF (open circuit): $m=1.540$ mg/sec and $t=6.4$ sec for $h=66$ cm. Benzhydryl bromide was always allowed to stand in DMF for at least 3 hr before being used. The oxygen dissolved in the solution was expelled by passing a stream of dry nitrogen through the cell solution for about 20 min prior to each electrolysis.

The Reaction of Benzhydryl Bromide with Mercury in a Degassed DMF Solution. A 0.10 M solution (50 m*l*) of tetraethylammonium perchlorate in DMF was degassed for 1 hr with nitrogen. To the solution, mercury (68.73 g, 342.6 mg-atom) and benzhydryl bromide (1.30 g, 5.26 mmol) were then added; the mixture was subsequently held at 25°C under a nitrogen atmosphere for 22.5 hr. The mercury was then separated from the reaction mixture, washed with water, dried *in vacuo*, and found to weigh 68.40 g (341.0 mg-atom). Hence, 1.6 mg-atom of mercury was consumed for its reaction with 5.26 mmol of the bromide. The DMF solution was concentrated by vacuum distillation, and the residue was taken up with benzene. The resulting solution was washed with water, dried with calcium chloride, and evaporated. The residue was recrystallized from *n*-hexane - benzene (4 : 1 by volume) to afford 0.366 g of *sym*-tetraphenylethane (mp 207—210°C; lit,[15] mp 211°C), the infrared spectrum of which was identical with that of an authentic sample. The mother liquor from the recrystallization was evaporated *in vacuo*, and the residue was chromatographed on alumina. Elution with *n*-hexane - benzene (9 : 1 by volume) afforded 0.033 g of additional *sym*-tetraphenylethane, mp 205—207°C (its identity was established by the infrared spectrum). The benzene fractions gave 0.062 g of benzophenone (mp 46—48°C; lit,[16] mp 49°C), which was identified by comparing its infrared spectrum with that of an authentic sample. The ether fractions afforded 0.326 g of benzhydrol (mp 65—67°C; lit,[16] mp 69°C), the infrared spectrum of which was identical with that of an authentic sample. From these results, the yields of *sym*-tetraphenylethane, benzophenone, and benzhydrol were estimated to be 46, 6, and 34% respectively.

The Reaction of Benzhydryl Bromide with Mercury in a DMF Solution Saturated by Oxygen. Dry air was bubbled into a mixture of 3.00 g (12.1 mmol) of benzhydryl bromide, 93.50 g of DMF, and 80.60 g of mercury for 280 min at room temperature. A white precipitate appeared. The reaction mixture was then filtered, and the filtrate was concentrated by vacuum distillation. When benzene was added to the residue, *ca.* 1 m*l* of insoluble liquid appeared; this was then separated. The benzene solution was washed with water, dried with magnesium sulfate, and evaporated *in vacuo*. By the recrystallization of the residue from methanol, 0.34 g

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of *sym*-tetraphenylethane was obtained (mp 206—208°C). The combined filtrates were evaporated *in vacuo* to give 1.97 g of an oily material, of which 0.96 g was chromatographed on alumina. *n*-Hexane fractions gave 0.10 g of crystals, which were fractionally recrystallized from ethanol to give 0.009 g of *sym*-tetraphenylethane (mp 195—201°C) and 0.079 g of dibenzhydryl ether (mp 101—105°C; lit,[17] mp 110°C; its identity was established by a study of the infrared spectrum). The benzene fractions gave 0.235 g of benzophenone (mp 44—48°C). The ether fractions gave 0.492 g of benzhydrol (mp 66—68°C). From these results, the yields of *sym*-tetraphenylethane, dibenzhydryl ether, benzophenone, and benzhydrol were estimated to be 18, 8, 24, and 45% respectively.

The Reaction of Benzhydryl Bromide with Mercury in a Benzene Solution. To a solution of 1.505 g (6.09 mmol) of benzhydryl bromide in 50 m*l* of benzene, 5 m*l* of mercury was added, and the resultant mixture was boiled under reflux for 9 hr. Gray solids precipitated. After the separation of the mercury, the reaction mixture was filtered. The residue was washed several times with hot benzene, and the combined benzene solution was evaporated *in vacuo* to give a viscous oil containing some white crystals; these crystals were recrystallized from benzene to give 0.659 g of *sym*-tetraphenylethane (mp 202—207°C). The mother liquor was evaporated *in vacuo*, and the residue was chromatographed on alumina. Elution with *n*-hexane gave 0.287 g of *sym*-tetraphenylethane (mp 205—207°C; total yield, 93%). The benzene fractions gave 0.001 g (0.1% yield) of benzophenone, and the ether fraction gave a trace of benzhydrol. Each of these products was identified by means of its infrared spectrum.

The gray solids precipitated from the reaction mixture were practically insoluble in DMF, too. However, when they were added to the solution of 2.56 g (12.2 mmol) of tetraethylammonium bromide in 100 m*l* DMF, they dissolved and the mercury was separated. The polarographic measurement of the resulting solution indicated that it contained 2.70 mmol of the tribromomercurate ion. This behavior of the gray solids is identical with that of mercurous bromide, which has been studied in the previous paper.[6] Hence, the yield of mercurous bromide was estimated to be 89%, based on the original bromide.

The Controlled Potential Electrolysis of Benzhydryl Bromide in DMF at −0.60 *V vs. SCE.* In a 1-*l* electrolytic cell, 300 m*l* of DMF, 6.87 g of tetraethylammonium perchlorate, and 50 m*l* of mercury were placed; the mixture was cooled to 2—4°C and degassed with nitrogen. Immediately after 0.366 g (1.48 mmol) of benzhydryl bromide had been added to the mixture, controlled potential electrolysis was started at −0.60 V *vs.* SCE. The quantity of electricity required for the complete electrolysis was estimated graphically from the current-time curve to be 0.00163 Faraday. The polarogram of the resulting catholyte agreed virtually completely with that of the bromide ion. The catholyte was concentrated by vacuum distillation and the residue was taken up in benzene. The benzene solution was washed with water, dried with calcium chloride, and evaporated. From the residue, 0.221 g (89% yield) of *sym*-tetraphenylethane (mp 205—206.5°C) and 0.029 g (8% yield) of benzophenone were isolated by fractional recrystallization and chromatography on alumina. Identity was established by a study of the infrared spectrum.

The Controlled Potential Electrolysis of Benzhydryl Bromide in DMF at −1.40 V vs. SCE. In a 1-*l* electrolytic cell, 300 m*l* of DMF, 6.87 g of tetraethylammonium perchlorate, and 50 m*l* of mercury were placed; the mixture was cooled to 2—4°C and degassed by a stream of nitrogen for 2 hr. Immediately after 0.344 g (1.39 mmol) of benzhydryl bromide had been added to the mixture, the resulting solution was electrolyzed at −1.40 V *vs.* SCE for 130 min. The quantity of electricity required for the complete electrolysis was estimated to be 0.00157 Faraday. The polarogram of the resulting catholyte agreed closely with that of the bromide ion. The catholyte was worked up exactly as in the previous experiment; 0.119 g (51% yield) of *sym*-tetraphenylethane (mp 210—212°C), 0.088 g (38% yield) of diphenylmethane (mp 25—26°C; lit,[16] mp 27°C) (identity established by a study of the infrared spectrum), and 0.012 g (5% yield) of benzophenone were thus obtained.

The Controlled Potential Electrolysis of Benzhydryl Chrolide in DMF at −2.13 V vs. SCE. A solution of 300 m*l* of DMF, 6.89 g of tetraethylammonium perchlorate, and 5.70 g (28.1 mmol) of benzhydryl chloride was degassed for 2 hr with pure nitrogen, and then electrolyzed at a controlled potential of −2.13 V *vs.* SCE. The current started at 7.5 A and fell to 0.026 A after 42.5 hr. The resulting catholyte was worked up exactly as in the previous experiment; 2.182 g (46% yield) of diphenylmethane (mp 25—26°C), 0.270 g (6% yield) of *sym*-tetraphenylethane (mp 206.5—207.5°C), 0.164 g (3% yield) of benzophenone, and 0.308 g (6% yield) of benzhydrol were thus obtained. Identity was established by a study of the infrared spectrum.

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