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Polarography of Halides in Dimethylformamide. V. Bromine and the Tribromide Ion

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The polarographic behavior of bromine and the tribromide ion at the dropping mercury electrode was investigated in dimethylformamide. A freshly-prepared solution of bromine gives two cathodic waves. When the solution is allowed to stand at 25°C in the dark, however, the first wave gradually becomes anodic, independently of the electrolysis. When the first wave is completely anodic, an equilibrium is established. The resulting polarogram coincides with that of hydrogen tribromide. The formation of hydrogen tribromide was ascribed to the chemical reduction of bromine by dimethylformamide. Diffuse sunlight accelerates the decomposition of bromine, which in turn yields hydrogen bromide. It was also suggested that, when the dropping mercury is used as an indicator electrode, bromine and the tribromide ion may react with the dropping mercury prior to being electrolyzed, forming mercuric bromide and the tribromomercurate ion respectively, which may in turn depolarize the indicator electrode.

The halogen-halide systems in non-aqueous solutions have been the subjects of a number of voltammetric studies. The solvents so far used include acetic acid,[1] acetic anhydride,[1] acetonitrile,[2-6] dimethylformamide (DMF),[7-11] dimethyl sulfoxide,[12,13] sulfolane,[14] and tetrahydrofuran.[15] In these solvents the trihalide ion (X_3^-) is so stable that the halogen species give two voltammetric waves, corresponding to the two redox reactions as follows:

$$3X_2 + 2e \rightleftharpoons 2X_3^- \qquad (1)$$

$$2X_3^- + 4e \rightleftharpoons 6X^- \qquad (2)$$

On the other hand, X_3^- is unstable in an aqueous solution, and X_2 gives only one reduction wave due to the reaction, as follows:[16]

$$X_2 + 2e \rightleftharpoons 2X^- \qquad (3)$$

Among the halogen-halide systems, the iodine-iodide system has been studied most extensively.[1-3,5-7,10-15] Fewer studies have been reported about the bromine-bromide[2,4,5,8,13,14] and the chlorine-chloride[2,9,13,14] systems, and none about the fluorine-fluoride system. The electrodes used in these investigations are made of platinum or pyrolytic graphite, each of which is inert to the halogen species. The dropping mercury electrode, which is reactive to the halogen species, has never been used for these studies.

In the present paper, the bromine-bromide system in DMF was investigated as part of a series of polarographic studies of halides in this medium.[17] The dropping mercury electrode was used as the indicator electrode. Sinicki and Bréant[8] have already studied the voltammetric behavior of bromine in DMF, using the platinum electrode. They have reported that a freshly-prepared solution of bromine gives two cathodic waves due to the reactions expressed by Eqs. (1) and (2). Using the dropping mercury electrode,

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[1] R. Guidelli and G. Piccardi, *Anal. Lett.*, **1**, 779 (1968).

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[8] C. Sinicki and M. Bréant, *Bull. Soc. Chim. Fr.*, **1967**, 3080.

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[17] Part IV: Y. Matsui and Y. Date, This Bulletin, **43**, 2052 (1970).

however, we found that the two cathodic waves given by a freshly-prepared solution of bromine may be explained in terms of the electrolytic reduction of the mercuric bromide formed by the reaction between the bromine and the mercury of the electrode prior to the electrolysis. Sinicki and Bréant[8] have also reported that bromine in DMF quantitatively converts to the tribromide ion on standing for a few hours, irrespective of the electrode process:

$$3Br_2 \text{ (in DMF)} \rightarrow 2Br_3^- \qquad (4)$$

This reaction is rather unusual in view of the fact that halogens or interhalogen compounds generally undergo disproportionation reactions in electron-donating solvents to yield the trihalide ions and the uni-positive halogen ions:[18-20]

$$2X_2 \rightleftharpoons X_3^- + X^+ \qquad (5)$$

They ascribed it to the reduction of bromine by formic acid, which was formed by the hydrolysis of DMF, but no experimental proof was presented. In the present paper, we also will examine the mechanism of the chemical reduction of bromine to the tribromide ion, and will suggest that the reductant may be not formic acid, but DMF.

Experimental

The DMF was purified as has been described previously.[21] The tetraethylammonium perchlorate (TEP) used as a supporting electrolyte was prepared and purified as has been described by Fujinaga *et al.*[22] Polyvinyl chloride (PVC) obtained commercially was used as a maximum suppressor. The bromine was dried over phosphorus pentoxide and was purified by distillation. Bp 57.8—58.1°C. Hydrogen bromide which had been generated from aqueous hydrobromic acid and concentrated sulfuric acid was passed through a glass tube packed with red phosphorus and was then bubbled through concentrated sulfuric acid. The dry hydrogen bromide thus obtained was dissolved in DMF. The resulting solution was standardized by titration against an aqueous sodium hydroxide solution, using phenolphthalein as the indicator. The solution of hydrogen tribromide in DMF was prepared by an equimolar addition of the hydrogen bromide solution to bromine. The solution of hydrogen tribromomercurate in DMF was similarly prepared from the hydrogen bromide and mercuric bromide.

D. c. polarography and conductivity measurements were carried out at 25°C as has been described previously.[23] All the potential measurements were done with reference to the aqueous saturated calomel electrode connected with the cell solution by a DMF-agar salt bridge.[22] The dropping mercury electrode used had the following characteristics in a 0.10 M solution of TEP in DMF (open circuit): $m=1.245$ mg/sec, $t=4.97$ sec for $h=66.0$ cm. 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.

Results

Variation in the Polarographic Characteristics of Bromine with the Time. The polarographic characteristics of bromine varied with the time. Figure 1 shows the polarograms recorded at several intervals after the addition of

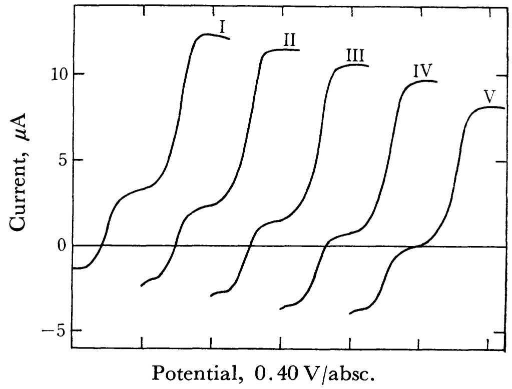

Fig. 1. Change of the polarogram of Br_2 (1.70 mM) with time in the dark. Each recording was started 0.8(I), 8.0(II), 25.0(III), 51.0(IV), or 161(V) minutes after addition of Br_2 to DMF.

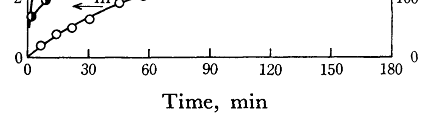

Fig. 2. Plots of the currents and the conductance *vs.* time for a Br_2 solution in the dark.

I, II and III: the limiting currents of the 1 st, 2 nd, and 3 rd waves of Br_2 (1.70 mM), respectively

I′: the anodic part of the 1 st wave

IV: the conductance of Br_2 (47.9 mM) in DMF

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[22] T. Fujinaga, K. Izutsu, K. Umemoto, T. Arai and K. Takaoka, *Nippon Kagaku Zasshi*, **87**, 105 (1968).

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

bromine to DMF containing 0.10 M TEP and 0.005% PVC. Since it was found that diffuse sunlight accelerates the change, as will be discussed later, the cell solution was placed in the dark. When the recording of the polarogram was started as soon as possible (45 sec) after the addition of bromine to a DMF solution, most of the two waves obtained were cathodic, although the first wave had already turned anodic in part. The anodic part of the first wave increased with the time at the expense of its cathodic part. When the first wave was completely anodic, an equilibrium was established. Parallel to this change, a new cathodic wave and a maximum arose and grew at about −1.33 and −2.15 V *vs.* SCE respectively (Fig. 6).

Figures 2 and 3 show the plots of the limiting currents and the half-wave potentials respectively *vs.* the time. The height of the second wave was approximately double that of the first wave, and both of them slightly decreased with the time. The height of the third wave increased with an increase in the anodic part of the first wave. An equilibrium was attained about two hours after the addition of bromine to DMF. Throughout these changes, however, the half-wave potential of each wave remained practically constant. The increase in the anodic part of the first wave obeyed good first-order kinetics (Fig. 4). The rate constant was determined to be 0.030 min^{-1} at 25°C.

The conductance of the bromine solution also increased with the time. The mode of increase in the conductance was analogous to that in the anodic current (Fig. 2). If bromine was added to DMF containing excess tetraethylammonium bromide, the conductance of the solution scarecely varied with the time (Fig. 5). No increase in the conductance with the time was observed until the molar concentration of the bromine added was higher than that of the bromide ion. This indicates that bromine rapidly reacts with the bromide ion, forming the tribromide ion, which is stable in DMF in the dark.

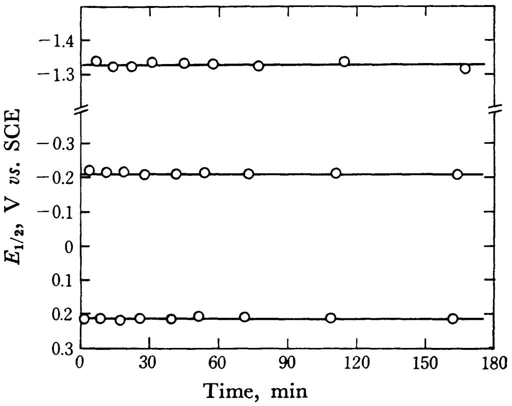

Fig. 3. Plots of the half-wave potentials *vs.* time for the three waves given by Br_2 in the dark.

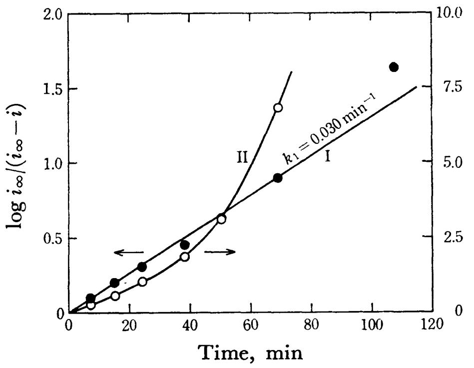

Fig. 4. The 1 st(I)- and 2 nd(II)-order rate plots for the increase of the anodic part of the 1 st wave given by Br_2.

the initial concn. of Br_2=1.70 mM

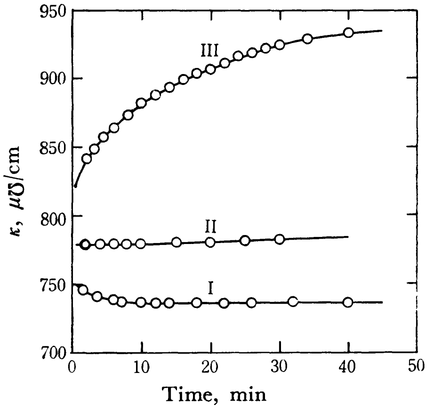

Fig. 5. Plots of the conductances *vs.* time for the various ratio of mixing between Br_2 and Et_4NBr.

$[Br_2]/[Et_4NBr]$=0.5(I), 1.1(II), and 1.8(III), where $[Et_4NBr]$=10.4 mM

Polarographic Behavior of Bromine, the Tribromide Ion, and Related Compounds. The polarogram of 1.0 mM bromine, which was recorded in the dark about two hours after it had been added to DMF, is shown in Fig. 6. The effects of the bromine concentration and of the height of the mercury reservoir on the polarographic characteristics are summarized in Tables 1 and 2 respectively. The heights of both the first and second waves were virtually proportional to the concentrations of the depolarizer and to the square roots of the heights of the mercury reservoir; this indicates that these waves are diffusion-controlled. The ratio between the diffusion-current constants (I_d's) of these waves is about 1.0 : 2.3. The characteristics of the third wave are somewhat more complicated. The height of this wave was practically proportional to the square root of the height of the mercury reservoir, but not to the con-

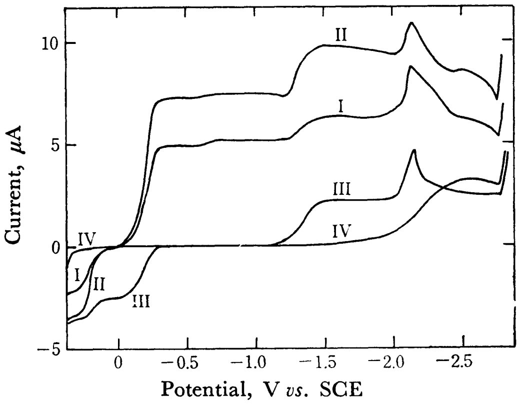

Fig. 6. Polarograms of 1.0 mM depolarizers in DMF containing 0.1 M TEP and 0.005% PVC at 25°C.

I, Br_2 recorded *ca.* 2 hr after the addition to DMF; II, HBr_3; III, HBr; IV, HCOOH

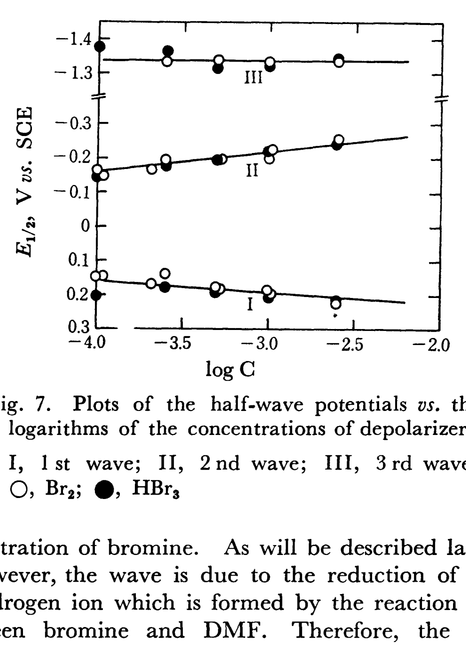

Fig. 7. Plots of the half-wave potentials *vs.* the logarithms of the concentrations of depolarizers.

I, 1st wave; II, 2nd wave; III, 3rd wave; ○, Br_2; ●, HBr_3

centration of bromine. As will be described later, however, the wave is due to the reduction of the hydrogen ion which is formed by the reaction between bromine and DMF. Therefore, the decrease in the diffusion-current constant may be due to the consumption of the hydrogen ion for the neutralization of such bases as dimethylamine present in solution as impurities.

With an increase in the concentration of bromine, the half-wave potential of the first wave shifted to a more positive direction, and that of the second wave, to a more negative direction, while that of the third wave remained virtually constant. Figure 7 shows the relation between the half-wave potentials of the waves ($E_{1/2}$) and the common logarithms of the concentrations of bromine (log *C*). Approximately linear relations were obtained between them with slopes of 0.030 V for the first wave, −0.060 V for the second wave, and 0.000 V for the third wave.

Figure 6 also shows the polarograms of hydrogen bromide, hydrogen tribromide, and formic acid in DMF. It is notable that hydrogen tribromide gives three polarographic waves closely similar to those of bromine recorded about two hours after it had been added to DMF. Hydrogen tribromomercurate also gave three waves similar to those of hydrogen tribromide. These data indicate that bromine converts to hydrogen tribromide in DMF and that the tribromide ion may react with mercury at the electrode surface, yielding the tribromomercurate ion, which may in turn depolarize the electrode. Formic acid gives no wave at the potential where the hydrogen ion is electrolytically reduced.

The polarographic characteristics of these depolarizers at various concentrations and at various heights of the mercury reservoir are summarized in Tables 3 and 4 respectively. All the heights of the first and second waves given by these depolarizers were practically proportional to the concentrations and to the square roots of the mercury heads; this indicates that they are diffusion-controlled. The height of the third wave of hydrogen bromide or of hydrogen tribromide was also proportional to the square root of the height of the mercury reservoir, but not to the concentration of the depolarizer, as had been observed for bromine. Hydrogen tribromomercurate gave no third wave until the concentration was as high as 2.1 mM. The relation between the half-wave potentials and the common logarithms of the concentration is plotted for hydrogen tribromide in Fig. 7. Approximately linear relations were obtained be-

TABLE 1. POLAROGRAPHIC CHARACTERISTICS OF BROMINE AT VARIOUS CONCENTRATIONS

Concn. (mM)	$E_{1/2}$ (V vs. SCE)			I_d		
	1 st wave	2 nd wave	3 rd wave	1 st wave	2 nd wave	3 rd wave
0.10	+0.147	−0.161	*	1.23	3.17	*
0.25	+0.141	−0.197	−1.332	1.49	3.42	0.11
0.50	+0.176	−0.194	−1.338	1.35	3.06	0.50
1.01	+0.207	−0.198	−1.335	1.36	3.00	0.63
2.52	+0.222	−0.258	−1.337	1.37	3.28	0.84

* No wave appeared.

TABLE 2. RELATION BETWEEN LIMITING CURRENTS OF 0.50 mM OF BROMINE AND EFFECTIVE HEADS OF THE DROPPING MERCURY ELECTRODE

$h_{corr.}$ (cm)	i_d, (μA)			$i_d/(h_{corr.})^{1/2}$		
	1 st wave	2 nd wave	3 rd wave	1 st wave	2 nd wave	3 rd wave
34.8	0.70	1.58	0.29	0.12	0.27	0.049
46.5	0.79	1.85	0.32	0.12	0.28	0.048
56.5	0.91	2.09	0.36	0.12	0.28	0.049
66.5	1.04	2.36	0.37	0.13	0.29	0.046
81.5	1.13	2.60	0.43	0.13	0.29	0.048

TABLE 3. POLAROGRAPHIC CHARACTERISTICS AT VARIOUS CONCENTRATIONS

Depolarizer	Concn. (mM)	$E_{1/2}$ (V *vs.* SCE)			I_d		
		1 st wave	2 nd wave	3 rd wave	1 st wave	2 nd wave	3 rd wave
HBr_3	0.10	+0.202	−0.145	−1.374	1.78	4.68	0.26
	0.26	+0.177	−0.177	−1.361	2.18	4.85	0.74
	0.51	+0.190	−0.194	−1.313	2.14	4.52	1.17
	1.02	+0.206	−0.215	−1.318	2.17	4.48	1.64
	2.55	+0.217	−0.244	−1.346	2.11	4.30	1.26
HBr	0.26	+0.156	−0.155	−1.310	0.67	1.56	0.11
	0.53	+0.175	−0.165	−1.359	0.51	1.39	0.86
	1.05	+0.203	−0.162	−1.317	0.58	1.40	0.86
	2.63	+0.229	−0.184	−1.309	0.60	1.32	1.17
	5.25	+0.233	−0.217	−1.390	0.60	1.31	1.27
$HHgBr_3$	0.25	+0.166	−0.176	*	1.58	4.00	*
	1.00	+0.189	−0.217	*	1.71	4.00	*
	2.50	+0.204	−0.240	−1.365	1.79	3.95	0.84

* No wave appeared.

TABLE 4. RELATION BETWEEN LIMITING CURRENTS OF 1.0 mM OF DEPOLARIZERS AND EFFECTIVE HEADS OF THE DROPPING MERCURY ELECTRODE

Depolarizer	$h_{corr.}$ (cm)	i_d (μA)			$i_d/(h_{corr.})^{1/2}$		
		1 st wave	2 nd wave	3 rd wave	1 st wave	2 nd wave	3 rd wave
HBr_3	34.8	2.39	4.22	1.86	0.41	0.75	0.32
	44.8	2.52	5.26	2.11	0.38	0.79	0.32
	54.8	3.05	6.16	2.23	0.41	0.83	0.30
	64.8	3.30	6.90	2.48	0.41	0.86	0.31
	79.8	3.70	7.52	2.75	0.41	0.84	0.31
HBr	34.8	0.72	1.65	1.05	0.12	0.28	0.18
	44.8	0.80	1.86	1.17	0.12	0.28	0.17
	54.8	0.84	2.09	1.27	0.11	0.28	0.17
	64.8	0.93	2.25	1.33	0.12	0.28	0.17
	79.8	1.03	2.50	1.46	0.12	0.28	0.16

tween them, similar to those obtained for bromine.

Figure 8 shows the effect of bromine, as well as those of mercuric bromide and tetraethylammonium bromide, on the electrocapillary curve in DMF containing 0.10 M TEP and 0.005% PVC. The addition of these compounds to DMF apparently caused a decrease in the surface tension of the mercury drop in the potential region between $+0.4$ and -0.5 V *vs.* SCE.

Effect of Diffuse Sunlight on the Change in the Polarogram of Bromine. Figure 9 shows the manner in which the growth of the anodic

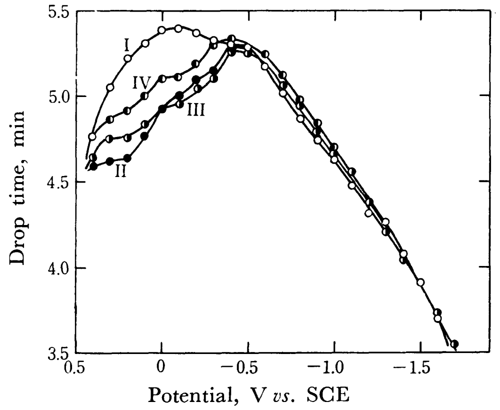

Fig. 8. Electrocapillary curves at 25°C.

I, 0.1 M TEP+0.005% PVC in DMF; II, I+1.0 mM Br_2; III, I+1.0 mM $HgBr_2$; IV, I+1.0 mM Et_4NBr

part of the polarographic wave, as well as the increase in the electric conductivity, of the bromine solution is accelerated by diffuse sunlight. The rate of the current increase abruptly slows down about 15 min after the addition of bromine to DMF. The resulting polarogram coincides with that of hydrogen tribromide. However, the tribromide ion is not so stable in diffuse sunlight as in the dark, and it slowly decomposed hereafter. Equilibrium was not established until both the first and second waves were completely anodic. The polarogram recorded after equilibrium was attained agreed with that of hydrogen bromide, as is shown in Fig. 6.

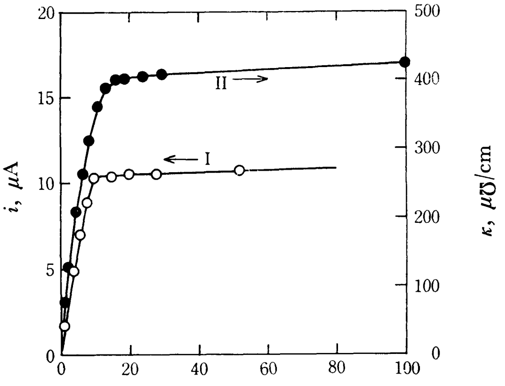

Fig. 9. Plots of the anodic part of the 1 st wave (I) and the conductance (II) *vs.* time for Br_2 solutions in the diffuse sunlight.

the initial concn. of Br_2=5.6 mM (I) or 10.0 mM (II)

Discussion

Mechanism of the Formation of Hydrogen Tribromide from Bromine in DMF in the Dark.

The conversion of the first wave of bromine from cathodic to anodic (Fig. 1) and the excellent agreement of the resulting polarogram with that of hydrogen tribromide (Fig. 6) indicate that bromine in DMF gradually forms hydrogen tribromide. This is supported by the fact that the conductance of the solution increases with an inrecase in the anodic part of the first wave (Fig. 2). The stoichiometry of this reaction is interesting. The height of each wave of 1.0 mM bromine measured about two hours after it is added to DMF is approximately equal to two-thirds of that of the corresponding wave of 1.0 mM hydrogen tribromide, which indicates that three moles of bromine quantitatively yield two moles of hydrogen tribromide in DMF:

$$3Br_2 + 2H\cdot(DMF) \rightarrow 2H^+ + 2Br_3^- \qquad (6)$$

This reaction is rather unusual, since it is well known that a disproportionation reaction occurs between two moles of halogen in electron-donating solvents, yielding one mole of the trihalide ion and one mole of the uni-positive halogen ion (Eq. (5)).[18-20] However, Reid and Muliken[18] have also reported that iodine in pyridine (Pr) forms the trihalide ion, together with the uni-positive iodine ion solvated by pyridine (PrI^+), which may in turn decompose to the iodide ion and the cation radical of pyridine ($Pr\cdot^+$) as follows:

$$Pr + PrI^+ \rightarrow I^- + 2Pr\cdot^+ \qquad (7)$$

Similar reactions have also been proposed by Zingaro *et al.*[24] Recently, Bist and Person[25] reported that a rapid reaction occurs between iodine and excess triethylamine in dioxane, yielding the iodide ion quantitatively as the end product. The reaction was ascribed to the reduction of the uni-positive iodine ion to the iodide ion by the amine. Thus, it can be considered that the following reaction may occur between bromine and DMF:

$$Br_2 \rightleftarrows Br^+ + Br^- \qquad (8)$$

$$Br^+ + 2DMF \rightarrow Br^- + 2DMF\cdot^+ \qquad (9)$$

$$2DMF\cdot^+ \rightarrow 2H^+ + 2R \qquad (10)$$

$$2Br_2 + 2Br^- \rightleftarrows 2Br_3^- \qquad (11)$$

The net result would be:

$$3Br_2 + 2DMF \rightarrow 2H^+ + 2Br_3^- + 2R \qquad (12)$$

In this reaction mechanism, Br_2 and Br^+ may be strongly solvated by DMF. The electron-transfer reaction from DMF to Br^+ has never been reported, but it is well known that DMF forms charge-transfer complexes with a number of Lewis acids. We have also found that DMF can reduce the simple mercuric ion, yielding metalic mercury.[17] The cation radical ($DMF\cdot^+$) thus formed may

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24) R. Zingaro, C. A. VanderWerf and J. Kleinberg, *J. Amer. Chem. Soc.*, **73**, 88 (1951).

25) H. D. Bist and W. B. Person, *J. Phys. Chem.*, **73**, 482 (1969).

rapidly decompose to the hydrogen ion and an unknown radical (R). Among the elemental reactions demonstrated above, either the disproportionation reaction (Eq. (8)) or, more probably, the electron-transfer reaction (Eq. (9)) may be the rate-determining step, for the kinetics of the total reaction is of the first-order (Fig. 4).

Sinicki and Bréant[8)] have attributed the quantitative formation of the tribromide ion to the reduction of bromine by formic acid, which had been formed by the hydrolysis of DMF. However, none of the polarograms of the DMF solutions in either the presence or absence of bromine gave any appreciable wave at −2.25 V *vs.* SCE, where formic acid gives a cathodic wave. Accordingly, it is unlikely that the formic acid plays a major role in the reduction of the uni-positive bromine ion. Michlmayr and Sawyer[13)] have reported that halogen may react with dimethyl sulfoxide and acetonitrile, yielding hydrogen halide, as follows:

$$X_2 + (CH_3)_2SO \rightarrow CH_2X(CH_3)SO + HX \tag{13}$$

$$X_2 + CH_3CN \rightarrow CH_2XCN + HX \tag{14}$$

However, according to these mechanisms, halogen does not quantitatively form the trihalide ion, but a part of it enters into combination with the carbon atoms of the solvents. Therefore, this is not the present case.

Effect of Diffuse Sunlight on the Reaction of Bromine in DMF. Diffuse sunlight accelerates the increase in the anodic part of the polarographic waves given by bromine. This rapid increase accompanies the rapid increase of the conductance of the solution (Fig. 9). The polarogram obtained after equilibrium is established is in accord with that of hydrogen bromide; this indicates that bromide is quantitatively reduced to the bromide ion in DMF. This behavior may be explained in terms of the following mechanism:

$$Br_2 \rightleftharpoons 2Br\cdot \tag{15}$$

$$Br\cdot + DMF \rightarrow H^+ + Br^- + R \tag{16}$$

$$Br^- + Br_2 \rightleftharpoons Br_3^- \tag{17}$$

$$Br_3^- \rightleftharpoons 2Br\cdot + Br^- \tag{18}$$

The net result would be:

$$Br_2 + 2DMF \rightarrow 2H^+ + 2Br^- + 2R \tag{19}$$

Mechanism of the Electrode Reaction of Bromine and the Tribromide Ion in DMF. The following electrode reaction mechanism has been proposed by Sinicki and Bréant[8)] for the reduction of bromine in DMF at the platinum electrode:

$$3Br_2 + 2e \rightleftharpoons 2Br_3^- \tag{20}$$

$$2Br_3^- + 4e \rightleftharpoons 6\,Br^- \tag{21}$$

A similar mechanism has also been offered by Michlmayr and Sawyer[13)] for the oxidation of hydrogen bromide in dimethyl sulfoxide at the platinum electrode. However, in the present study the dropping mercury electrode was used as the indicator electrode, and it is reactive to both bromine and the tribromide ion. If the heterogeneous reactions between mercury and bromine, and between mercury and the tribromide ion, are very rapid, the formation of mercuric bromide and of the tribromomercurate ion may precede the electrode reactions. Thus, the following mechanisms can be considered for bromine:

(Chemical process)

$$Br_2 + Hg \rightarrow HgBr_2 \tag{22}$$

(Electrode process)

$$3HgBr_2 + 2e \rightleftharpoons Hg + 2HgBr_3^- \tag{23}$$

$$2HgBr_3^- + 4e \rightleftharpoons 2Hg + 6Br^- \tag{24}$$

and for the tribromide ion:

(Chemical process)

$$Br_3^- + Hg \rightarrow HgBr_3^- \tag{25}$$

(Electrode process)

$$2HgBr_3^- + Hg \rightleftharpoons 3HgBr_2 + 2e \tag{26}$$

$$2HgBr_3^- + 4e \rightleftharpoons 2Hg + 6Br^- \tag{27}$$

These mechanisms are supported by the fact that the polarographic characteristics of bromine and the tribromide ion are closely similar to those of mercuric bromide and the tribromomercurate ion respectively. The electrocapillary curve of the solution of bromine in DMF was also very similar to that of mercuric bromide. Sinicki and Bréant[8)] have reported that the tribromide ion in DMF gives two waves, anodic and cathodic, at +0.57 and −0.46 V *vs.* Hg/Hg(II) at the platinum electrode. The difference (1.03 V) in the half-wave potential between these two waves is much greater than that observed at the dropping mercury electrode (0.40 V). This may be caused either by the irreversibility of the electrode reaction at the platinum electrode or, more probably, by the difference between the depolarizers in the two cases.

In any case, however, the relations between the current (i) and the potential of the dropping mercury electrode (E) should be expressed for the first wave of the tribromide ion or of bromine measured after equilibrium is attained as:[23)]

$$E_p = C_p + (\boldsymbol{RT}/2\boldsymbol{F})\ \ln i^3/(i_d - i)^2 \tag{28}$$

and for the second wave as:

$$E_n = C_n - (\boldsymbol{RT}/2\boldsymbol{F})\ \ln i^3/(i_d - i) \tag{29}$$

where i_d is the limiting current and where C_p and C_n are constants. The results of the logarithmic plot for the waves of the tribromide ion, as well as those for bromine (Fig. 10), show that Eqs. (28) and (29) hold for these depolarizers. The reciprocal slopes of the logarithmic plots are equal to 0.032—0.035 V for the first wave and to −0.040—−0.041 V for the second wave. Both of the values are somewhat larger than the theoretical

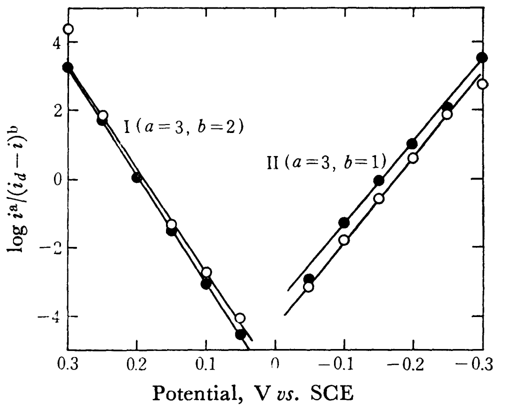

Fig. 10. Analysis of the polarograms of 1.0 mM Br_3^- (●) or of 1.0 mM Br_2 measured *ca.* 2 hr after it was added to DMF (○).

reciprocal slopes; I(●), 0.032 V; II(●), −0.041 V; I(○), 0.035 V; II(○), −0.040 V

value (0.030 V), but virtually agree with those obtained for the waves of the tribromomercurate ion (0.032 and −0.038 V respectively[23]).

From Eqs. (28) and (29), the following relations between the half-wave potentials ($E_{1/2}$) and the limiting currents (i_d), or between $E_{1/2}$ and the concentrations (C) of the tribromide ion or of bromine, can easily be derived for the first wave:

$$E_{p,1/2} = C_p' + (\boldsymbol{RT}/2\boldsymbol{F}) \ln C \qquad (30)$$

and for the second wave:

$$E_{n,1/2} = C_n' - (\boldsymbol{RT}/\boldsymbol{F}) \ln C \qquad (31)$$

Fig. 5 shows that these relations also hold for the depolarizers.

No close examination was made of the maximum which appeared at −2.15 V *vs.* SCE on the polarograms of hydrogen tribromide and hydrogen bromide. However, it was found that no maximum arose on the polarograms with tetraethylammonium tribromide, but that a maximum appeared on the polarogram with hydrogen perchlorate. This clearly indicates that the hydrogen ion is responsible for the maximum.