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Voltammetric Study of Organic Metals. I. The Determination of the Electrochemical Conditions for Crystal Growth

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The metallic crystals of organic charge-transfer complexes are grown by means of the electrolytic oxidation of tetrathiafulvalene (TTF) derivatives in the presence of trihalide anions in organic solvents. In order to obtain a crystal of good quality, the optimal conditions for the growth have been searched for based on the data on the cyclic voltammetry. In this paper, the electrochemical conditions, such as the oxidation potential, the stability of the donor monocation radicals, and the redox behavior of the anions under the oxidation potential of the donors, are discussed in relation to the chemical reactions proceeding in the solution during the crystal growth.

The metal-like crystals (organic metals) of organic charge-transfer complexes have various interesting characteristics, such as electrical[1)] and optical[2)] anisotropies and metal-insulator phase transitions.[3—5)] Especially, some of the organic metals obtained from bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and tetramethyltetraselenafulvalene (TMTSF) with several inorganic anions have been found to become superconductors at low temperatures,[6,7)] so that numerous physicists and chemists have been concentrating their attention on the crystals of their organic charge-transfer complexes. Therefore, it is extremely important to establish a systematic way of growing crystals of good quality so as to explore their physical properties and develop a new category of electronic materials. There have appeared, hitherto, four methods of crystal growth; by means of slow cooling,[8)] condensation,[9)] diffusion,[10)] and electrocrystallization.[11)] The crystal growth of organic metals or superconductors, which are composed of organic donors and inorganic anions, has thus far been obtained mainly by the electrocrystallization. The electrocrystallization is carried out by the electrochemical oxidation of the donor in the presence of supporting electrolytes in various organic solvents.

There are many kinds of counter-anions used for the crystallization of organic metals. From among these, trihalide anions with a linear structure have now been investigated, because the chemical nature of the trihalides can be gradually changed from Cl_3^- to I_3^- depending on the combination of the components.

Usually, an electrolytic reaction in a solution has been controlled under constant-current conditions (not under constant voltage conditions). However, it has not yet been clarified whether or not the crystal growth has thereby been carried out under optimal conditions, since the chemical reactions occurring at the electrodes are complicated. This problem will be discussed in this paper based on the data obtained by the cyclic voltammetry (CV) of the donors (D) and the trihalide anions (X^-).

Experimental

Electrochemical Measurement. The measurement of CV was carried out with a Fuso 312 polarograph and a Hokuto HB-104 function generator. The working and counter electrodes were a platinum disk (2 mmϕ) and a platinum wire (0.5 mmϕ, 3 cm) respectively. The supporting electrolyte was 0.1 M (M=mol dm^{-3}) tetrabutylammonium perchlorate (Bu_4NClO_4). An aqueous SCE was used as a reference electrode with a salt bridge of 0.1 M Bu_4NClO_4 dissolved in organic solvents. The measuring temperature was controlled at 25±0.1 °C. Tetrahydrofuran (THF) and benzonitrile (BN) were chosen as convenient solvents for CV, because in them both the donors and the supporting electrolyte were easily dissolved. When THF was used as a solvent, nitrogen gas saturated beforehand with a THF vapor was bubbled in order to remove the dissolved oxygen.

Crystal Growth. All the crystal-growth procedures employed were similar to the following example. 0.13 mmol (BEDT-TTF) was electrolytically oxidized in a 60-ml THF solution, in which 0.52 mmol Bu_4NI_3 had been dissolved, under a controlled current of 1 μA at 20 °C. The electrolysis was performed under an atmosphere of nitrogen gas. The working electrode was separated with a porous glass plate from the counter electrode; both were of platinum. The period of crystal growth was about 1—1.5 months.

Reagents. The TMTSF was purchased from Japan Carlit Co., Ltd. The TTF, BEDT-TTF, tetrakismethylthiotetrathiafulvalene (TMT-TTF), and bis(trimethylenedithio)tetrathiafulvalene (BTDT-TTF) were obtained from Tokyo Kasei Co., Ltd. The tetramethyltetrathiafulvalene (TMTTF) was synthesized by the coupling of 4,5-dimethyl-1,3-dithiolium perchlorate.[12)] The Bu_4NX (X=Br_2Cl, $BrCl_2$, and Cl_3) were obtained from Tokyo Kasei Co., Ltd. The other tetrabutylammonium trihalides were synthesized by the addition reaction of tetrabutylammonium halides and halogens.[13,14)] The donors and the supporting electrolytes were purified by recrystallization. The THF was purified as follows: powdered iron(II) sulfate was added to the solvent, and the mixture was stirred; if the color of the powder turned from green to brown, the old powder was replaced with a new one. This treatment was repeated until the green coloring of iron(II) persisted. Then the powder was removed by filtration. The solvent was dehydrated by adding NaOH pellets for 12 hours. The solvent was then filtered and distilled. BN was purified as follows: After the solvent had been dried by adding powdered phosphorous pentoxide for 12 hours, the desiccant was removed by decantation; powdered anhydrous sodium carbonate was then added to the solvent, and the mixture was stirred for 3 hours. The solvent was filtered and distilled under a reduced pressure.

Results and Discussion

In the electrolytic crystallization, organic metals can be grown from the de-electronated D^+ and the dissolved X^-. In this process, information on the oxidation potential of D to D^+, the stability of D^+, and the electronic state of X^- at the oxidation potential of D is essential in order to obtain good crystals. Therefore, the electrolytic oxidation and reduction behavior of D and X^- have been studied in detail with CV.

If the electron-transfer process at the electrode is reversible, the oxidation potential (E_p^o) obtained by means of CV is more positive by $28.5/n$ mV than the standard oxidation potential (E^o), where n is the number of participating electrons.[15] On the other hand, the E_p^o value of the irreversible process shifts toward more positive values than that of the reversible case, depending on degree of irreversibility. The E_p^o value for irreversible cases is, therefore, only a semi-quantitative measure of the oxidizability. If both the oxidation peak and the re-reduction peak are observable, the mean value of these two peaks, $E^{o\prime}$, can be conveniently used as the effective potential, which is near E^o.

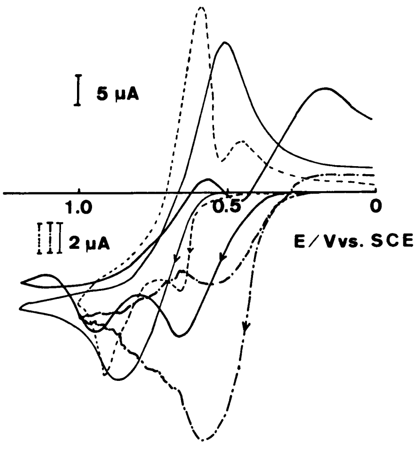

Fig. 1. Cyclic voltammograms of the donors in THF; 20 mV s^{-1}.
——: 5.88 mM TTF, —·—·—; 3.48 mM TMTTF, ———: 2.40 mM TMT-TTF, ······: 2.20 mM BTDT-TTF.

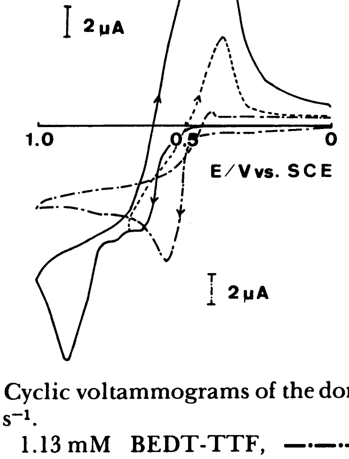

Fig. 2. Cyclic voltammograms of the donors in THF; 20 mV s^{-1}.
——: 1.13 mM BEDT-TTF, —·—·—: 1.26 mM TMTSF.

Electrolytic Oxidation of D. Generally, the electrode reaction of TTF derivatives occurs as a two-step oxidation process; in the first step, one electron is transferred, and then the second electron is transferred. The corresponding reduction processes occur in the reversed way:[16]

$$D \underset{+e,\, E_p^{r1}}{\overset{-e,\, E_p^{o1}}{\rightleftarrows}} D^+ \underset{+e,\, E_p^{r2}}{\overset{-e,\, E_p^{o2}}{\rightleftarrows}} D^{2+} \qquad (1)$$

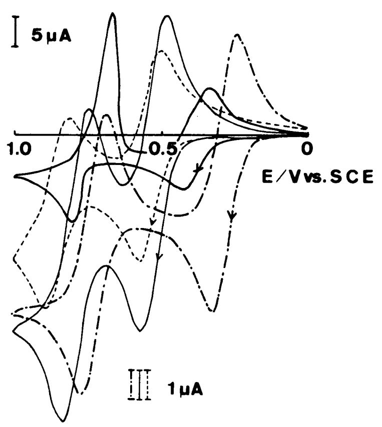

Fig. 3. Cyclic voltammograms of the donors in BN; 20 mV s^{-1}.
——: 2.77 mM TTF, —·—·—: 2.05 mM TMTTF, ———: 2.83 mM TMF-TTF, ······: 1.62 mM BTDT-TTF.

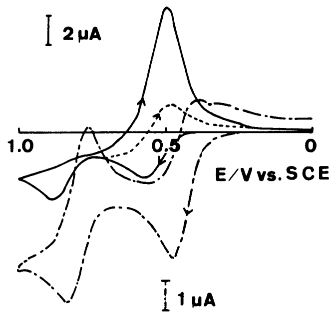

Fig. 4. Cyclic voltammograms of the donors in BN; 20 mV s^{-1}.
——: 1.25 mM BEDT-TTF, —·—·—: 1.41 mM TMTSF.

Table 1. Electrochemical Data of Various Donors (E/V vs. SCE, 20 mV s^{-1})

Solvent	Donor	E_p^{o1} D→D$^+$	E_p^{o2} D$^+$→D^{2+}	$E^{o\prime}$	$\lvert E_p^{r1}-E_p^{o1}\rvert = \Delta E$	i_p^{r1}/i_p^{o1}	$\lvert E_p^{o1}-E_p^{o2}\rvert = \Delta E_p$
THF	TTF	0.67	0.95	0.44	0.47	0.79	0.28
	TMTTF	0.59	0.75$^{a)}$	0.40	0.39	b)	0.16
	TMT-TTF$^{c)}$	0.88	d)	0.71	0.35	0.86	—
	BEDT-TTF	0.65	0.90	0.51	0.29	0.63	0.25
	BTDT-TTF	0.66	0.91	0.58	0.16	0.09	0.25
	TMTSF	0.56	0.80	0.47	0.18	0.40	0.24
BN	TTF	0.43	0.79	0.39	0.09	1.00	0.36
	TMTTF	0.32	0.77	0.28	0.08	1.00	0.45
	TMT-TTF	0.57	0.83	0.53	0.08	0.88	0.26
	BEDT-TTF	0.57	0.84	0.51	0.13	0.63	0.27
	BTDT-TTF	0.58	0.89	0.54	0.08	0.79	0.31
	TMTSF	0.48	0.84	0.44	0.08	0.53	0.36

a) Shoulder. b) Very small value. c) The adsorption on the electrode was very strong. d) No wave was found until 1.2 V.

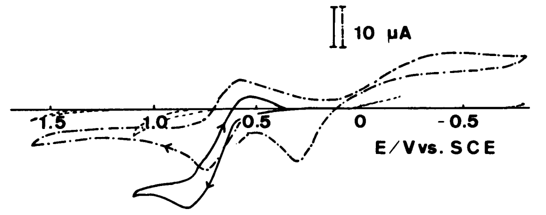

Fig. 5. Cyclic voltammograms of Bu$_4$NI$_3$; 20 mV s^{-1}. ——: 8.4 mM Bu$_4$NI$_3$ in THF, —·—·—: 6.5 mM Bu$_4$NI$_4$ in BN, ······: blank.

Figures 1—4 show the CV measurements for TTF derivatives; the results are summarized in Table 1. It may be noted that the value of $\Delta E(=\lvert E_p^{o1}-E_p^{r1}\rvert)$ is the measure of the reversibility, which should be ≈60 mV for a reversible one-electron transfer process. In BN, the donors were oxidized quasi-reversibly to monocations (ΔE≈80 mV). On the contrary, in THF, the donors were irreversibly oxidized; ΔE varies from 0.47 V to 0.16 V with an increase in the molecular weights of the donors. Though the irreversible reactions were carried out in THF, $E^{o\prime}$ can be obtained since re-reduction peaks were observed. It can be readily estimated whether or not the oxidation reaction really occurs under the applied potential from the E_p^{o1}, E_p^{o2}, and $E^{o\prime}$ values in Table 1. It seems that the pair of TMTTF and TMTSF, and the pair of BEDT-TTF and BTDT-TTF, which have very similar structures to each other, give similar CV profiles and similar oxidation potentials. No meaningful correlation of E_p^{o1} with the molecular weight of donors is found, however, as is plotted in Fig. 6.

In the electrolytic crystal growth, the applied potential should not exceed E_p^{o2} if only D$^+$ is to be generated in the solution.

The instability of D$^+$ can be judged from the CV data based on the following two viewpoints: i) If the ΔE value is large and the re-reduction peak is much distorted, or if the ratio of i_p^{r1}/i_p^{o1} is extremely small, then D$^+$ is chemically unstable and can easily be changed to other products. Therefore, most of the D$^+$ in BN are stable, while most of the D$^+$ in THF are unstable (Table 1). ii) D$^+$ is oxidized further to D^{2+} under relatively high potentials. If the value of $\Delta E_P(=\lvert E_p^{o1}-E_p^{o2}\rvert)$ is large, the proportionation reaction:

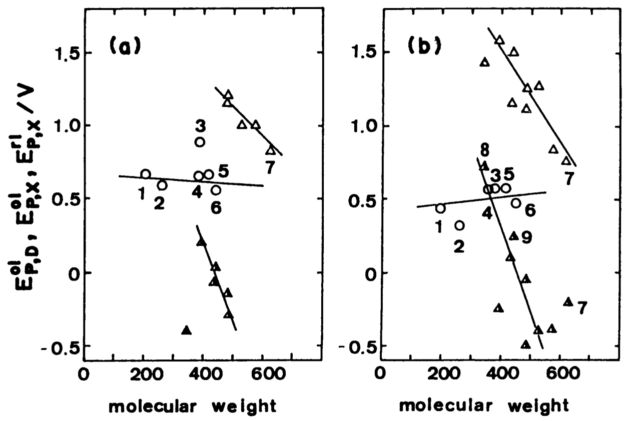

Fig. 6. Plots of E_p^{o1} of D, and $E_{p,X}^{o1}$ and $E_{p,X}^{r1}$ of X$^-$ vs. the molecular weight. (a), in THF; (b), in BN. (○), $E_{p,D}^{o1}$; (△), $E_{p,X}^{o1}$; (▲), $E_{p,X}^{r1}$ 1: TTF, 2: TMTTF, 3: TMT-TTF, 4: BEDT-TTF, 5: BTDT-TTF, 6: TMTSF, 7: I$_3^-$, 8: Cl$_3^-$, 9: BrCl$_2^-$.

$$\mathrm{D^{2+} + D \rightarrow 2D^{+}} \qquad (2)$$

proceeds to the right and the D^{2+} will be transformed to D$^+$. Therefore, most of the D^{2+} in BN may be changed to D$^+$, while some of the D^{2+} in THF seem to persist in the solution and may become a cause of crystal defects or disorders.

Electronic State of Trihalide Anions in the Solution. As for the electrolytic crystal growth, the applied potential (E) must be an intermediate value between the oxidation peak potential ($E_{p,X}^{o1}$) and the reduction peak potential ($E_{p,X}^{r1}$) of X$^-$ in order to keep X$^-$ unchanged in the solution; of course, E should be more positive than the oxidation peak potential of D, $E_{p,D}^{o1}$, to generate D$^+$. Typical voltammograms for I$_3^-$

are shown in Fig. 5, while the results are summarized in Table 2. Figure 6 presents the plots of $E^{o1}_{p,X}$ and $E^{r1}_{p,X}$ vs. the molecular weight (MW) of the trihalide anions. The oxidation and reduction potentials of X^- decrease with an increase in the MW of trihalide anions; this can reasonably be understood by considering that the oxidation potential of halide anions decreases with an increase in MW, as $Cl^- > Br^- > I^-$ (Table 3). In Fig. 6 the plots of $E^{o1}_{p,D}$ vs. MW are also shown. Most trihalide anions were stable under the oxidation potential of D, except for the following cases.

Exception 1: When TMT-TTF is electrolytically oxidized in a THF solution containing I_3^-, the crystal growth is difficult, for such by-products from I_3^- as I_2 are produced[17]; the E^{o1}_p of TMT-TTF in THF is more positive than the E^{o1}_p of I_3^-. In a BN solution, Cl_3^- is reduced easily under the oxidation potential of the donors.

Exception 2: Generally, trihalide anions composed of lighter elements more easily decomposed in the organic solvent. Figure 7a shows the decomposition of $BrCl_2^-$ in THF. The reduction wave detected at 0.20 V in the first scan gradually decreased upon the repeated scanning, and eventually it disappeared. Moreover, a new oxidation wave appeared at 0.7 V on the disappearance of the yellow coloring in the solution; this new wave corresponds to the oxidation of Br^- (Table 3). These results suggest that $BrCl_2^-$ decomposes to other products containing Br^-. Since Cl_3^- is extremely unstable, the CV measurement in THF was difficult. Figure 7b shows such a situation; the CV peaks disappeared very rapidly on successive scannings. Figure 8 shows the change in the UV absorption spectra of Bu_4NCl_3 in THF after the dissolution of the reagent in the solution; the decrease in the absorption spectra may show the decomposition of Cl_3^- to Cl_2 and Cl^-, since the addition of Cl^- was found to suppress the change.

Crystal-Growth Conditions. As a typical case, we have carried out the electrocrystallization from BEDT-TTF and trihalide ions under constant current conditions; the results are summarized in Table 4.

Table 2. Oxidation and Reduction Peak Potentials of Trihalide Anions (E/V vs. SCE, 20 mV s^{-1})

X^- of $Bu_4N^+X^-$	in THF E^{o1}_p	in THF E^{r1}_p	in BN E^{o1}_p	in BN E^{r1}_p
I_3^-	0.83	—	0.75	−0.20
I_2Br^-	1.00	—	0.83	−0.38
IBr_2^-	1.00	—	1.28	−0.40
$IBrCl^-$	1.20	−0.30	1.25	−0.50
ICl_2^-	b)	0.02	1.50	0.25
Br_3^-	1.15	−0.15	1.11	−0.05
Br_2Cl^-[a]	b)	−0.07	1.15	0.10
$BrCl_2^-$[a]	b)	0.20[a]	1.58	−0.24
Cl_3^-[a]	b)	−0.40[a]	1.44	0.72

a) Very unstable and easily decomposed. b) More positive than 1.2 V.

Table 3. Oxidation Peak Potentials of Halide Anions (E/V vs. SCE, 20 mV s^{-1})

X^- of $Bu_4N^+X^-$	in THF E^{o1}_p	in BN E^{o1}_p
I^-	0.37	0.32
Br^-	1.00	0.72
Cl^-[a]	—	1.35

a) The adsorption on the electrode was very strong.

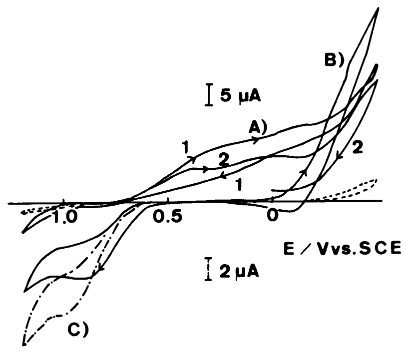

Fig. 7a. Cyclic voltammograms of 11.5 mM Bu_4NBrCl_2 in THF; 20 mV s^{-1}. (A), The yellow solution: the first scan 1) and the second scan 2); (B), after the color of the solution disappeared; (C), the voltammogram of 5.7 mM Bu_4NBr in THF.
……: blank.

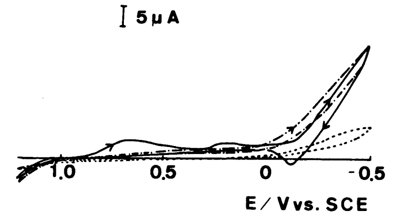

Fig. 7b. Cyclic voltammograms of 7.4 mM Bu_4NCl_3 in THF; 20 mV s^{-1}.
———: the first scan, —·—·—: the second scan, ·······: blank.

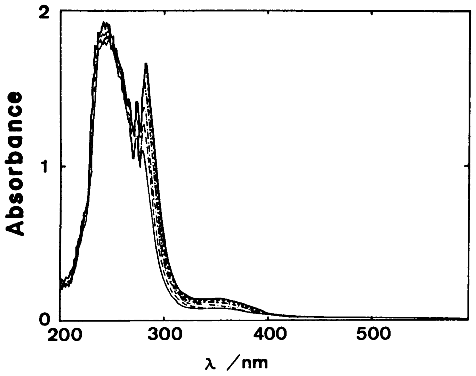

Fig. 8. UV absorption spectra of 0.76 mM Bu_4NCl_3 in THF (Time is in minute after dissolution of the salt).
———: 0 min, ········: 1.65 min, —·—·—: 5.07 min, —·—·—: 10.07 min, ······: 14.57 min, ———: 22.40 min.

Table 4. Results of the Electrocrystallization of BEDT-TTF with Trihalides[a]

X^- of $Bu_4N^+X^-$	In THF day	In THF i/μA	In THF E/V	In THF Size[b] /mm×mm	In BN day	In BN i/μA	In BN E/V	In BN Size[b] /mm×mm
I_3^-	29	1.0	1.0	3.5×1.5	40	1.0	1.2	2.0×2.0
I_2Br^-	44	1.0	1.0	3.0×2.5	33	1.0	0.2	3.3×2.0
IRr_2^-	44	2.0	1.0	4.0×1.1	45	1.0	0.3	8.9×1.9
$IBrCl^-$	54	1.0	0.3	Powder	32	1.0	0.2	1.4×0.1
ICl_2^-	49	1.0	0.3	1.9×0.3[c]	32	1.0	0.1	Powder
Br_3^-	17	1.0	0.2	Powder	—			d)
Br_2Cl^-	—			d)	—			d)
$BrCl_2^-$	—			d)	—			d)
Cl_3^-	—			d)	—			d)

a) The data are taken from *Synth. Met.*, **19**, 611 (1987). b) The thickness is not measured. c) Only at the bottom of the crystal-growth cell. d) No crystals were obtained.

When the current was set at 1 μA, the apparent voltage between the two electrodes[11] became 0.3—1.2 V, depending on the D, the X^-, and the solvents. Because our cells for the electrocrystallization had been prepared so as to obtain a crystal of the highest purity and to avoid any impurities such as water molecules diffused from the reference electrode, it is practically impossible to introduce a reference electrode to measure the rigorous potential at each electrode. In spite of such a restriction on the experimental system, from our experimental results we can derive some conclusions that are essential to the crystal growth of the BEDT-TTF complexes.

As is shown in Table 4, we could not obtain any trace of the crystal from BEDT-TTF with Cl_3^-, $BrCl_2^-$, and Br_2Cl^- in either THF or BN, or with Br_3^- in BN. This result is reasonably explained by the above-mentioned unstable nature of the trihalide anions composed of lighter halogens, which leads to the production of Cl_2 and Br_2 by their decomposition. Before BEDT-TTF is electrolytically oxidized, these dihalogen molecules react with BEDT-TTF and/or the solvent; moreover, unnecessary oxidation and reduction reactions occur in the solution, which prevent the formation of the aimed-at crystals.

In the case of a BEDT-TTF–I_3^- system in THF, crystals of a good quality and a proper size were obtained, whereas in the case of a TMT-TTF–I_3^- system, it was difficult to obtain crystals,[18] possibly because of the oxidation of I_3^- in THF under the oxidation potential of TMT-TTF. On the other hand, in the case of the TMT-TTF–I_3^- system in BN, the crystal growth was very difficult,[18] although I_3^- is electrolytically stable in BN. The reason for this must be left to a forthcoming study.

Summary

The electrolytic oxidation and reduction behavior of donors (D=TTF, TMTTF, TMT-TTF, BEDT-TTF, BTDT-TTF, and TMTSF) and trihalide anions (X^-=I_3^-, I_2Br^-, IBr_2^-, $IBrCl^-$, ICl_2^-, Br_3^-, Br_2Cl^-, $BrCl_2^-$, and Cl_3^-) in organic solvents (THF and BN) were clarified by means of cyclic voltammetry.

It was found that 1) radical cations (D^+) of most of the donors were stable in BN, but unstable in THF, and 2) most trihalide anions (X^-) were stable under the oxidation potential of D, with a few exceptions.

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