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# Application of Electrochemical Recycle of $Ti^{4+}$-$Ti^{3+}$ to Additive Dimerization of Butadiene with Hydroxylamine

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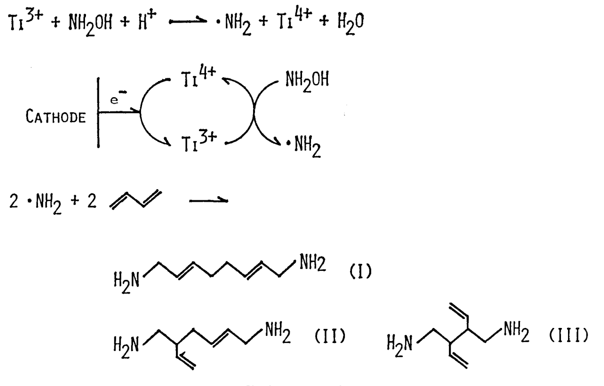
The electrolytic recycle of $Ti^{4+}$-$Ti^{3+}$ has been employed for a redox-system consisting of hydroxylamine and $Ti^{3+}$ which can produce amino radicals. From electroanalytical measurements, it was found that titanium(IV) chloride in hydrochloric methanol was reducible to $Ti^{3+}$ with a sufficient current efficiency at the platinum electrode and the reduction was speeded up by an addition of hydroxylamine. On macro-scale electrolysis using a small amount of titanium(IV) chloride in the presence of 1,3-butadiene and hydroxylamine, the generated amino radical undergoes additive dimerization with butadiene and gives diaminooctadienes in reasonable yields.

The action of titanium(III) chloride on hydroxylamine in acid solution brings about the formation of an amino radical.[1] Previously, Coffman and his co-workers[2] showed that the amino radical generated in this way gave rise to additive dimerization with olefins to form the corresponding diamines. In these processes, one mole of titanium(III) chloride is consumed per mole of hydroxylamine, because $Ti^{4+}$ produced in the redox-system cannot be rereduced by hydroxylamine. On the other hand, the electrocatalytic mechanism for the regeneration of $Ti^{3+}$ from $Ti^{4+}$ in the presence of hydroxylamine has been studied by different electroanalytical techniques,[3] but in most cases, oxalic acid was used as radical scavenger. Here we have examined the applicability of the $Ti^{4+}$-$Ti^{3+}$ recycle by means of electrochemical reduction to Coffman's method, as depicted in Scheme 1.



Scheme 1.

$Ti^{3+}$ produced by the cathodic reduction of titanium(IV) chloride reduces hydroxylamine to amino radical along with the oxidation of itself to $Ti^{4+}$. The generated amino radical attacks 1,3-butadiene followed by additive dimerization to give diaminooctadienes, whereas the resulting $Ti^{4+}$ undergoes rereduction at the cathode. According to the above recycle, this reaction is expected to occur sufficiently even when a small amount of titanium(IV) chloride is used.

Analogous processes, indirect electrochemical reductions which employ low-valent transition metal ions as a mediator, have been reviewed by Dietz and Lund.[4]

## Results and Discussion

In the preliminary experiments, current-potential measurements were carried out on 2 M hydrochloric methanol, in both the presence and absence of titanium(IV) chloride.

As can be seen in Fig. 1, when a mercury pool was used as the cathode, the hydrochloric methanol without titanium(IV) chloride was not reduced below the potential of −1.1 V (SCE). An addition of hydroxylamine to the catholyte showed a similar current-potential curve; therefore, its reduction potential should be approximately −1.1 V or more cathodic. Hydrochloric methanol containing titanium(IV) chloride showed two reduction waves: the first wave was at −0.15 V and the

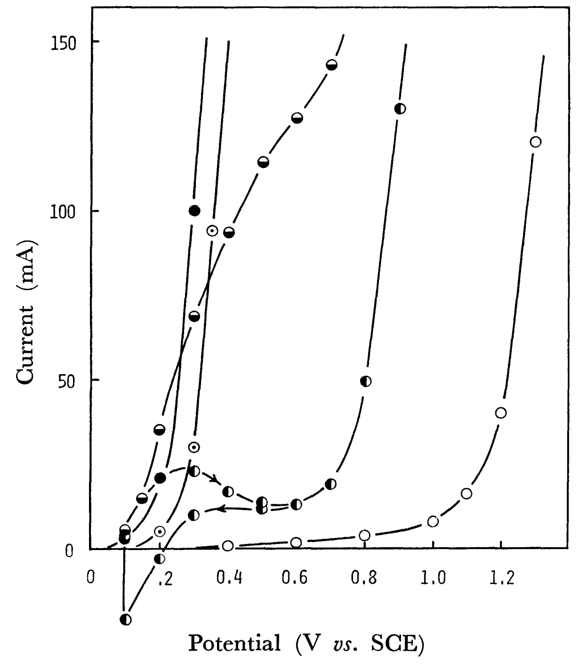


Fig. 1. Plots of current vs. cathode potential:
The relationships between current and potential were recorded automatically (sweep rate of 50 mV/s was used) but to economize on space tracings were prepared for reproduction herein. The measurements were carried out in 2 M HCl-MeOH at 25 °C.
a) On mercury; -○- in the absence and presence of $NH_2OH \cdot HCl$ (0.06 M), -◐- stationary curve in the presence of $TiCl_4$ (0.05 M), -◒- initial curve recorded immediately after adding $NH_2OH \cdot HCl$ (0.06 M). b) On platinum; -⊙- in the absence and presence of $NH_2OH \cdot HCl$ (0.06 M), -●- in the presence of $TiCl_4$ (0.05 M),

Table 1. Analytical results of $Ti^{3+}$ generated on Pt cathode[a)]

| No. | Catholyte | | Constant current (A) | Consumed current (mF) | Cathode potential (V *vs.* SCE) | Conversion Found/Theoretical (%) |
|---|---|---|---|---|---|---|
| | $TiCl_4$ (mmol) | HCl-MeOH 80 ml | | | | |
| 1 | 9.3 | 2 M | 1.0 | 3.1 | 0.21—0.26 | 80 |
| 2 | 9.3 | 2 M | 1.0 | 6.2 | 0.20—0.30 | 64 |
| 3 | 9.3 | 2 M | 1.0 | 9.3 | 0.21—0.35 | 56 |
| 4 | 9.3 | 2 M | 0.5 | 3.1 | 0.19—0.23 | 84 |
| 5 | 9.3 | 2 M | 0.5 | 6.2 | 0.19—0.31 | 73 |
| 6 | 9.3 | 2 M | 0.5 | 9.3 | 0.18—0.35 | 67 |
| 7 | 9.3 | 2 M | 0.2 | 9.3 | 0.13—0.33 | 74 |
| 8 | 9.3 | 0.5 M | 1.0 | 9.3 | 0.21—0.36 | 49 |
| 9 | 18.6 | 2 M | 1.0 | 9.3 | 0.19—0.26 | 71 |
| 10 | 18.6 | 5 M | 1.0 | 9.3 | 0.20—0.28 | 71 |

a) Electrolyses were carried out in an ice bath. For volumetric determination of $Ti^{3+}$, the electrolysis solution was directly titrated with standard $FeCl_3$ solution in nitrogen atmosphere.

second was at —0.80 V. Further, an oxidation wave was observed on the anodic sweep in the vicinity of —0.15 V, which corresponded to the oxidation of the first reduction peak. It would arise from a reversible charge transfer of titanium ions. In polarographic studies,[5)] it has been confirmed that a mixture of titanium(IV)–titanium(III) chlorides in dilute hydrochloric acid showed a cathodic half-wave potential of —0.80 V where the $Ti^{4+}$-$Ti^{3+}$ couple did not behave reversibly; however, in relatively concentrated solutions of hydrochloric acid, the wave was markedly shifted to a more positive position and was close to —0.15 V. Accordingly, the second wave may be attributed to the irreversible reduction of $Ti^{4+}$.

Under conditions of controlled potential electrolysis of titanium(IV) chloride in hydrochloric methanol at —0.3 V, the catholyte soon changed to a blue color, which suggests the occurrence of $Ti^{3+}$, and hence the first wave described above was undoubtedly exhibited by the reduction of $Ti^{4+}$ to $Ti^{3+}$. Later, on addition of hydroxylamine to the catholyte, the electrolytic current suddenly increased, accompanied by a color change from blue to yellow. These observations indicate that $Ti^{3+}$ is consumed for the reduction of hydroxylamine as soon as it is formed, and that the presence of hydroxylamine results in an acceleration of the cathodic reduction of $Ti^{4+}$ by an electrocatalytic mechanism.

On the other hand, when platinum was used as the cathode, titanium(IV) chloride in hydrochloric methanol was reduced at a potential of —0.15 V, whereas the hydrochloric methanol alone initiated the reduction at —0.25V. Owing to the insignificant difference between the two potentials, platinum seemed entirely unsatisfactory as the generator cathode of $Ti^{3+}$. However, as shown in Table 1, titanium(IV) chloride was effectively reduced to $Ti^{3+}$ even at the low concentration at the platinum cathode, although hydrogen evolution was observed at the end of the electrolysis. In fact, Malmstadt and Roberts[6)] reduced titanium(IV) chloride at a platinum cathode with 100% current efficiency in hydrochloric acid greater than 7 M. Since platinum was found to be available as the cathode, the mercury cathode was not used for macro-scale electrolysis, in spite of its much greater hydrogen overvoltage, because it is troublesome to handle.

On the basis of the electroanalytical results, preparative electrolyses were conducted under several conditions at the platinum cathode.

Figure 2 shows the results of constant current electrolyses of hydrochloric methanol containing hydroxylamine, 1,3-butadiene, and various amounts of titanium(IV) chloride. When the mol ratio of titanium(IV) chloride to hydroxylamine was more than 0.2, diaminooctadienes were obtained in yields of *ca.* 60% based on hydroxylamine. Immediately before the end of the electrolyses, namely, when the current

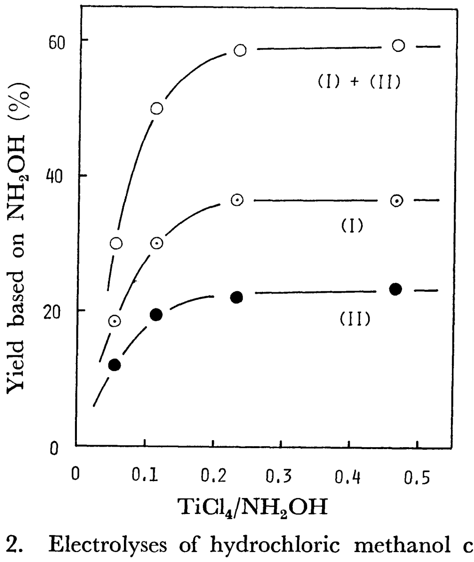


Fig. 2. Electrolyses of hydrochloric methanol containing hydroxylamine, butadiene, and various amounts of titanium (IV) chloride:

Catholyte: $NH_2OH \cdot HCl$, 36 mmol; $C_4H_6$, 180 mmol; 2 M HCl-MeOH, 80 ml. Constant current, 1.0 A. Consumed current, 37.3 mF.

(I) $H_2N\text{-}CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2\text{-}NH_2$

(II) $H_2N\text{-}CH_2CH(\text{-}CH{=}CH_2)CH_2CH{=}CHCH_2\text{-}NH_2$

was consumed in slight excess of the quantity of electricity required to convert hydroxylamine, the catholyte assumed a blue color. This indicates that the reduction of $Ti^{4+}$ and the subsequent reaction of $Ti^{3+}$ with hydroxylamine proceed almost quantitatively. Consequently, under these conditions, the material yield would be governed by the reactivity of the amino radical with butadiene rather than the current efficiency for the generation of $Ti^{3+}$, although a certain amount of titanuim ions would be inactivated.

In the present reaction, three kinds of isomers of diaminooctadiene were considered, but (III) could not be detected in our experiments. The relative amounts of (I) and (II) were invariably 62:38. This is in agreement with the results in free radical polymerizations of 1,3-butadiene, in which the 1,4-addition reaction is more favorable than the 1,2-addition.[7]

Figure 3 shows the relationships among the consumed current, the current efficiency, and the product yield. The current efficiency for the formation of diamines linearly decreased with the increase of the consumed current, whereas the material yield based on hydroxylamine increased below the consumed current of 50 m farady (the theoretical extent of conversion of hydroxylamine is 67%), but above this value diamines were no longer produced.

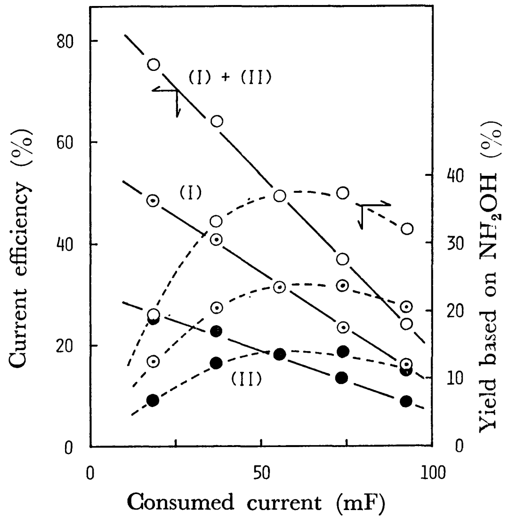


Fig. 3. The relationships among the current efficiency, consumed current, and the product yield:
Catholyte: $TiCl_4$, 9.3 mmol; $C_4H_6$, 72 mmol; $NH_2OH \cdot HCl$, 72 mmol; 2 M HCl-MeOH, 80 ml. Constant current, 1.0 A.

From the results in Figs. 2 and 3, $Ti^{4+}$ is presumed to be rereduced 4—5 times on the electrode. Moreover, it is probable that water produced as the reaction proceeds renders $Ti^{4+}$ inactive and gives rise to the side reaction. In fact, an addition of water to the catholyte greatly inhibited the electrolysis for the formation of diamines and caused the precipitation of titanium salt, gas evolution, and adhesion of tarry materials on the cathode.

Figure 4 shows the dependence of the amount of butadiene on the product yield. The use of a large excess of butadiene showed a tendency to increase the formation of materials with a high boiling point which were soluble in acidic solution. Thus it is probable that polymerization would occur. On the contrary, by the use of less than the theoretical amounts, for example, when the mol ratio of butadiene to hydroxylamine was 0.5, the yield of diaminooctadienes based on butadiene increased to over 90%.

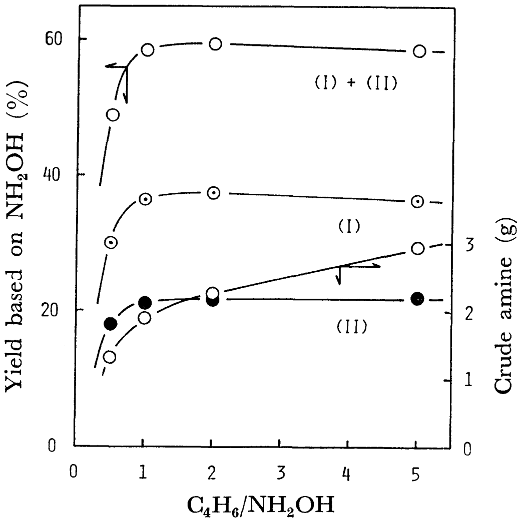


Fig. 4. The dependence of the amount of butadiene on the product yield:
Catholyte: $TiCl_4$, 9.3 mmol; $NH_2OH \cdot HCl$, 36 mmol; 2M HCl-MeOH, 80 ml. Constant current, 1.0 A. Consumed current, 37.3 mF.

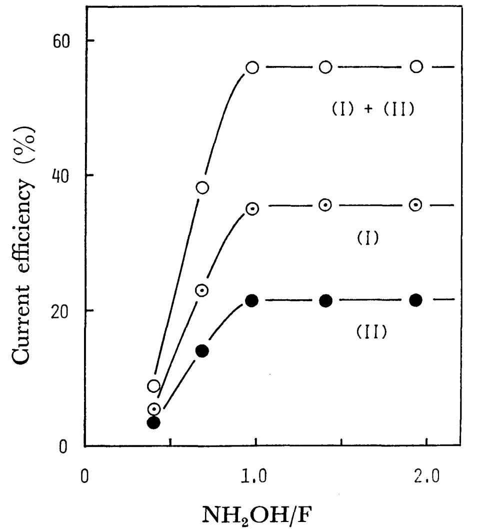


Fig. 5. The dependence of the amount of hydroxylamine:
Catholyte: $TiCl_4$, 9.3 mmol; $C_4H_6$, 180 mmol; 2 M HCl-MeOH, 80 ml. Constant current, 1.0A. Consumed current, 37.3 mF.

Furthermore, as shown in Fig. 5, the product yield was hardly affected by even significant amounts of hydroxylamine, but was dependent on the consumed current. In order to run the electrolysis effectively, therefore, equimolar amounts of butadiene and hydroxylamine should be used.

## Experimental

*Reagents.* Titanium(IV) chloride was purified by distillation after heating over mercury. Reagent grade hydroxylamine hydrochloride and 1,3-butadiene were used without purifications. Hydrochloride methanol was prepared by passage of dry hydrochloride through distilled methanol.

*Apparatus.* The instrument used to control potential and current for electroanalytical studies was a Nichia HP-E500H type potentiostat and a constant current unit. The electrode potential was scanned by means of a Nichia S-5A type potential programer. The relationship between current and potential was recorded on a Yokogawa 3077 X-Y recorder. Large scale electrolyses were performed with a Yanagimoto VE-8 potentiostat.

Current-potential measurements were made at 20 °C in a two-compartment H-type cell with a glass frit separating the compartments. The main compartment (25 ml) was provided with a working electrode (a smooth platinum plate or mercury pool, each area is 4 $cm^2$), a nitrogen gas bubbler, gas outlet, and a sce reference electrode. The other compartment (15 ml) contained a platinum wire as a counter electrode. All potentials were referred to the saturated calomel electrode.

Constant current electrolyses for preparative studies were carried out in a 100 ml-separable flask shielded from the anode compartment by a porous cup, and a reflux condenser (−10 °C) was connected to the cathode compartment. A cylindrical platinum net (4.5 cm in height, 11.0 cm in circumference, 55 mesh) was used at the cathode and the anode was a coil of platinum wire (0.8 mm$\phi$, 20 cm). The reference electrode was situated adjacent to the working electrode when necessary. The cell was cooled with ice water and nitrogen was bubbled through the cell during electrolysis.

*Analytical.* The amines were identified titrimetrically and spectroscopically. The amino nitrogen was analyzed by titration with perchloric acid in acetic acid in the usual manner. IR and mass spectra were recorded on a Hitachi 295 spectrophotometer and a Hitachi M-52 mass spectrometer, respectively. $^1H$-NMR spectra were measured with a Hitachi 20A spectrometer using $CDCl_3$ as the solvent. Chemical shifts are given in ppm from TMS as the internal standard. Gas chromatographic analyses were conducted with a Hitachi 163 gas chromatograph using a 2-m glass column packed with 20% Apieson grease and 10% potassium hydroxyde on a 60—80 mesh Chromosorb W AW, a column temperature of 170 °C (preheater 200 °C), and a flow rate of 40 ml/min (nitrogen gas). Retention times for (I) and (II) isomers were 13.5 and 10.0 min, respectively.

For volumetric determination of $Ti^{3+}$ generated cathodically, the electrolysis solution was directly titrated with 1.0 M ferric chloride in nitrogen atmosphere.

*Electrolyses for Preparative Studies.* A typical experimental procedure is as follows. The catholyte contained 36 mmol of $NH_2OH \cdot HCl$, 37 mmol of butadiene, and 9.3 mmol of $TiCl_4$ dissolved in 80 ml of 2 M HCl–MeOH. The electrolysis was carried out under a constant current at 1.0 A for 1 h. After the electrolysis, the blue catholyte was evaporated under reduced pressure. Then the residue was poured into a strong alkaline solution, and was extracted twice with a 20 ml portion of ether. The combined extracts were analyzed by GLPC. Analytical samples were obtained by fractional distillation. (I): Bp 91—94 °C/3 mmHg; IR (neat) $\nu$ 3370, 3280, 1600 ($NH_2$), 970 $cm^{-1}$ (*trans* C=C); NMR ($CDCl_3$) $\delta$ 1.2 (4H, $-CH_2-N\underline{H}_2$), 2.1 (4H, $-C\underline{H}_2-CH=$), 3.2 (4H, $=CH-C\underline{H}_2-NH_2$), 5.5 ppm (4H, $-CH_2-C\underline{H}=C\underline{H}-CH_2-$); *MW* 140 (mass); Found: neut. equiv., 69.5. Calcd for $C_8H_{16}N_2$: neut. equiv., 70.1. (II): Bp 74—75 °C/3 mmHg; IR (neat) $\nu$ 3370, 3280, 1640, 1600 ($NH_2$), 970 (*trans* C=C), 910 $cm^{-1}$ (term. vinyl); NMR ($CDCl_3$) $\delta$ 1.1 (4H, $-CH_2-N\underline{H}_2$), 2.1 (3H, $=CH-C\underline{H}_2-C\underline{H}-CH=$), 2.6 (2H, $-CH-C\underline{H}_2-NH_2$), 3.2 (2H, $=CH-C\underline{H}_2-NH_2$), *ca.* 5 (2H, $-CH=C\underline{H}_2$), 5.5 ppm (3H, $-CH_2-C\underline{H}=C\underline{H}-CH_2-$, $-C\underline{H}=CH_2$); *MW* 140 (mass); Found: neut. equiv., 69.8. Calcd for $C_8H_{16}N_2$: neut. equiv., 70.1.

## References

1) a) P. Davis, M. G. Evans, and W. C. E. Higginson, *J. Chem. Soc.*, **1951**, 2563; b) H. Seaman, P. J. Taylor, and W. A. Waters, *ibid.*, **1954**, 4690; see also, Z. Yoshida, T. Matsumoto, and R. Oda, *Kogyo Kagaku Zasshi*, **65**, 46 (1962); Z. Yoshida, T. Matsumoto, and R. Oda, *ibid.*, **67**, 64, 67, 70, 72, 76 (1964); S. Maiti and M. K. Saha, *J. Polym. Sci. A-1*, **5**, 151 (1967); T. Kakurai, T. Sugata, and T. Noguchi, *Kobunshi Kagaku*, **25**, 120 (1968).

2) C. J. Albisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner, and W. E. Mochel, *J. Am. Chem. Soc.*, **81**, 1489 (1959).

3) a) A. Blažek and J. Koryta, *Collect. Czech. Chem. Commun.*, **18**, 326 (1953); b) P. Delahay, C. C. Mattax, and T. Berzins, *J. Am. Chem. Soc.*, **76**, 5319 (1954); c) O. Fischer, O. Dracka, and E. Fischerova, *Collect. Czech. Chem. Commun.*, **26**, 1505 (1961); d) J. H. Christie and G. Lauer, *Anal. Chem.*, **36**, 2037 (1964); e) H. B. Herman and A. J. Bard, *ibid.*, **36**, 510 (1964); f) P. J. Lingane and J. H. Christie, *J. Electroanal. Chem.*, **13**, 227 (1967). *Cf.* T. H. Ridgway, R. P. Van Duyne, and C. N. Reilley, *ibid.*, **34**, 267 (1972).

4) R. Dietz and H. Lund, "Organic Electrochemistry," ed by M. M. Baizer, Marcel Dekker, Inc., New York (1973), Chap. 24. For the industrial importance, *cf.* R. Clarke, A. Kuhn, and E. Okoh, *Chem. Britain*, **11**, 59 (1975); and B. Kastening, International Symposium on Industrial Electrochemistry, Indian Institute of Technology, Madras, India, Dec., 1976, Abstruacts, p. 95.

5) J. J. Lingane and J. H. Kennedy, *Anal. Chim. Acta*, **15**, 294 (1956); see also, R. Strubl, *Collect. Czech. Chem. Commun.*, **10**, 475 (1938); M. Kolousek, *ibid.*, **11**, 592 (1939); R. Tamamushi, *Bull. Chem. Soc. Jpn.*, **23**, 220 (1950).

6) a) P. Arthur and J. F. Donahue, *Anal. Chem.*, **24**, 1612 (1952); b) H. V. Malmstadt and C. B. Roberts, *ibid.*, **27**, 741 (1955).

7) F. E. Condon, *J. Polym. Sci.*, **11**, 139 (1953).