Inhibition Effects of Cyclopentadiene Derivatives on the Iron Corrosion in Sulfuric Acid

Hiroshi Nishihara* and Kunitsugu Aramaki*

*Faculty of Science and Technology, Keio University

Inhibition effects of cyclic dienes and trienes on the iron corrosion in 1 N sulfuric acid were investigated by polarization measurements. Cyclopentadiene and its derivatives, indene and fluorene showed strong inhibition effects even at low concentrations. The inhibition efficiency of indene at 10^{-6} M was 82%. Polarization curves suggested the formation of stable iron- η^5 -cyclopentadienyl bonds by the oxidative-addition reaction on the surface. Inhibition efficiency of indene increased gradually with time, while that of 1,3-cyclooctadiene decreased. The amounts of above two compounds consumed on the iron surface were larger than those used for the monolayer coverage. These results suggested that the polymerization reaction played a significant role in addition to the formation of the stable iron- η^5 -indenyl bond for the large inhibition effect of indene.

1. Introduction

It has been known that organic compounds with π bonds have corrosion inhibition effects^{(1)~(8)}. Simple olefins inhibit the cathodic reaction of iron corrosion in acid solution⁽¹⁾, probably because of their electron back-donation ability. Although many kinds of π -bondings between a metal and a charged ligand have been shown in organometallic chemistry, the activity of charged π -acids as corrosion inhibitors has scarcely been reported. The η^5 -cyclopentadienyl ligand, which forms a stable bond with transition metals, is a monovalent anion. In the reactions of cyclopentadiene with transition metals or their complex ions, the oxidative-addition of the C-H bond often occurs to give η^5 -cyclopentadienyl complexes^{(9)~(14)}. Of our interest are the problems whether cyclopentadiene and its derivatives form metal- η^5 -cyclopentadienyl bonds by reacting with corroding metal surfaces and how that bonds function in their mechanism of corrosion inhibition.

We describe here the inhibition effects of cyclic dienes and trienes including cyclopentadiene derivatives on the iron corrosion in sulfuric acid investigated mainly by polarization measurements, and discuss the existence of metal- η^5 -cyclopentadienyl bonds on the iron surface.

2. Experimental

2.1 Corrosion inhibitors

Cyclopentadiene (abb. Cp) and its derivatives, indene (In), fluorene (F1), pentamethylcyclopentadiene (PMCP), sodium pentacarbomethoxycyclopentadienide ($\text{Na}^+\text{PCMCp}^-$), azulene (Az) were used as inhibitors (see Fig. 1). Other cyclic dienes and trienes, 1,3-cyclohexadiene (1,3-CHD), cycloheptatriene (CHT), 1,3- and 1,5-cyclooctadienes (1,3-COD and 1,5-COD), and 1,5,9-cyclododecatriene (CDT) were also tested. Benzene (Bz) and naphthalene (Nap) were used in order to examine the inhibition effects of benzene rings. $\text{PMCP}^{(15)}$ and $\text{Na}^+\text{PCMCp}^{(16)}$ were prepared in the same manner as previously reported. Others were obtained from commercial sources and purified by distillation or recrystallization before use. Decomposition rates of the inhibitors in 1 N sulfuric acid were measured at $30 \pm 0.1^\circ\text{C}$ with a UV spectrometer, Nihonbunko UVIDEC-610A.

2.2 Polarization measurements

The electrode was a 99.99% iron rod (5.0 mm ϕ , obtained from Johnson-Matthey Chemicals, Pb: 0.003%, Mg < 0.0001%, Mn < 0.0001%, Si < 0.0001%) embedded in a Teflon rod. Its surface was abraded with No. 2000 emery paper, cleaned ultrasonically in acetone, rinsed with water, and immersed in 50 ml of the deaerated corrosive solution. Polarization measurement was carried out potentiostatically after 1 h immersion using a

* 3-14-1, Hiyoshi, Kohoku-ku, Yokohama, 223 Japan

Fig. 1 Corrosion inhibitors.

Hokuto HA-104 potentiostat with a Pt counter electrode and an SCE reference electrode at $30 \pm 0.1^\circ\text{C}$.

2.3 Weight loss measurements

An iron plate (20 mm $\times$ 40 mm $\times$ 0.5 mm, purity 99.7%) was abraded with No. 1000 emery paper, cleaned ultrasonically in acetone, washed with water, and immersed in 120 ml of the deaerated corrosive solution. Test was carried out at $30 \pm 0.1^\circ\text{C}$ for 1 h, 2 h and 3 h.

2.4 Adsorbed inhibitor measurements

Reduced iron powder (Merck, surface area: 0.39 m²/g) was added into a 1 N sulfuric acid with a inhibitor, In or 1,3-COD, and the change of the UV spectrum of the solution was monitored for 1 h. The amount of inhibitors adsorbed on the iron powder was calculated from the absorbance-time curve (*vide infra*).

3. Results

Stabilities of cyclic dienes and trienes were examined in 1 N sulfuric acid. The decomposition rate increased in the order, 1,5-COD $\approx$ 1,5,9-CDT $<$ Fl $<$ In $<$ Cp $<$ CHT $\ll$ PMCP. The decomposition product of PMCP exhibited no effects on the iron corrosion.

The potential-time curves of the iron electrode in the solutions with Cp and CHT are shown in Fig. 2. In the solution of Cp the rest potential was less noble by 40 mV than that in the solution without inhibitors. On the contrary, the rest potential in the CHT solution settled near that in the case of no inhibitor after 1 h immersion.

Polarization curves of the iron electrode in 1 N sulfuric acid with cyclic dienes and trienes are classified into two groups, A and B, by the difference of cathodic Tafel slopes. The slope in the solution of inhibitors in group A is similar to that in the solution without inhibitors, and the degree of slope in the solution of inhibitors in

Fig. 2 Potential-time curve of Fe in 1 N H₂SO₄ with inhibitors. ^aCp at 1.1×10^{-4} M. ^bCHD at 1.9×10^{-3} M. ^cCHT at 5.1×10^{-5} M.

group B is larger than that in the solution without inhibitors. The inhibitors in group B include Cp, In and Fl (see Fig. 3), and the other cyclic dienes and trienes are involved in group A. The compounds in group A were effective mainly on the inhibition of the cathodic reaction, and the rest potential of the electrode in the solution of these compounds was near that in the solution without inhibitors. In Fig. 3 is represented the polarization curve of the electrode in the solution of CHT as an example of the inhibitors in group A. On the contrary, in the solution of Cp, the rest potential of the electrode was less noble than that in the solution without inhibitors, and both the anodic and cathodic processes were inhibited. The effect on the cathodic reaction increased in the order,

Fig. 3 Polarization curves of Fe in 1 N H₂SO₄ with inhibitors. ^aCp at 1.1×10^{-4} M. ^bIn at 6.8×10^{-5} M. ^cFl at 2.6×10^{-6} M. ^dCHT at 1.9×10^{-3} M.

Fig. 4 Inhibition efficiency of cyclic dienes and trienes for Fe corrosion in 1 N H_2SO_4 . ^aCp. ^b1,3-CHD. ^cCHT. ^d1,3-COD. ^e1,5-COD. ^f1,5,9-CDT. ^g $\text{Na}^+\text{PCMCP}^-$. ^hIn. ⁱFl. ^jAz. ^kBz. ^lNap.

$\text{Cp} < \text{Fl} < \text{In}$, and the effect on the anodic reaction was similar to that for the compounds in group B.

Relations of inhibition efficiency with inhibitor concentration are shown in Fig. 4. Inhibition efficiency, $I_p(\%)$, was calculated from Eq. (1),

$$I_p = (1 - i_{\text{corr}}/i_{\text{corr}}^0) \times 100 \quad (1)$$

where i_{corr} and i_{corr}^0 are the corrosion current densities for the inhibited and uninhibited electrode, respectively. Cyclopentadiene (Cp) and its derivatives, In, Fl and Az, showed higher inhibition efficiencies at low concentration compared with the other dienes and trienes. The inhibition effect of $\text{Na}^+\text{PCMCP}^-$ appeared on the anodic reaction only at the concentration more than 10^{-2} M.

Polymerization of the inhibitor in the solution or on the iron surface must give an influence on the corrosion inhibition effect. Then changes of inhibition efficiency were examined for Cp, In and 1,3-COD by weight loss measurements. Inhibition efficiency, I_w , for the first, second and third one hour from the moment of the immersion was calculated from Eq. (2),

$$I_w = (1 - w/w^0) \times 100 \quad (2)$$

where w and w^0 are the weight losses for the inhibited and uninhibited test piece, respectively. The values of I_w were obtained in the time intervals of first, second and third one hour, respectively. Results are shown in Fig. 5. Increase of the inhibition efficiency was found for In and decrease for 1,3-COD with time.

The amount of In or 1,3-COD adsorbed on the

Fig. 5 Change of inhibition efficiency with time. ^aCp at 2.9×10^{-3} M. ^bIn at 1.1×10^{-4} M. ^c1,3-COD at 3.4×10^{-4} M.

Fig. 6 Change in UV absorbance of inhibitor in 1 N H_2SO_4 by addition of Fe powder. ^aThe value is obtained by dividing the absorbance at time $t(A_t)$ by that at time zero (A_0). ^bTime zero is the moment of iron addition.

iron surface was calculated by the difference between the UV absorbance at the wave length of the peak band of the inhibitor in 1 N sulfuric acid before addition of the iron powder and that obtained by the extrapolation of the absorbance-time curve to the moment of iron addition. Results are shown in Fig. 6. Using the covering area of the

inhibitor obtained by projection of the molecular model on a plane ($S(\text{In})=46 \text{ \AA}^2$; $S(1,3\text{-COD})=48 \text{ \AA}^2$), the number of the ratio, $n=(\text{the amount of adsorbed inhibitor on the iron surface at the moment of iron addition})/(\text{the amount of adsorbed inhibitor which forms the monolayer on the surface})$ were calculated. The ratio, n , was ca. 1.5 for In and ca. 4 for 1,3-COD.

4. Discussion

The inhibitors Cp, In and Fl showed different inhibition activities for the iron corrosion from other cyclic dienes and trienes. Their inhibition efficiencies were higher than others even at low concentrations, implying stronger bondings of cyclopentadiene derivatives with iron than the other cyclic dienes and trienes. Formation of stable iron- η^5 -cyclopentadienyl bonds is most likely for explaining the difference. In a strong acid solution, Cp, In and Fl exist as diene form because of their weak acidity (pK_a of Cp: 18.0, In: 20.1, Fl: 22.6)¹⁷⁾, then a hydrogen abstraction from a cyclopentadiene ring is needed for the formation of iron- η^5 -cyclopentadienyl bond. We consider that the hydrogen abstraction is possible since cyclopentadiene derivatives are relatively facile to take an oxidative-addition reaction with transition metals to form a metal- η^5 -cyclopentadienyl bonds^{13), 14)} as shown in Eq. (3).

Corrosion inhibition by the oxidative-addition has recently found by using benzyl halide¹⁸⁾. In the inhibition by benzyl halide, where both η^3 -benzyl and halide ligands were expected to bind to iron, the polarization curve of an iron electrode showed two distinctive features; one was a shift of the rest potential towards the noble one and the other was a large inhibition of the cathodic reaction. Since both the features were found in the polarization curve of the electrode in the solution of Cp, the oxidative-addition of cyclopentadiene to iron and the formation of iron- η^5 -cyclopentadienyl bond were confirmed. Further study on the possibility and the detail mechanism of the formation of metal- η^5 -cyclopentadienyl bond in the electrochemical system is now in progress by using iron-diene and iron-triene complexes.

A cyclopentadiene derivative, $\text{Na}^+\text{PCMCp}^-$, did not exhibit a strong inhibition effect. Bruce *et al.*¹⁹⁾ have identified that PCMCp^- cannot co-

ordinate to a transition metal through a cyclopentadienyl ring but through carbomethoxy groups. The result that the Na^+PCMp^- inhibited only in the anodic reaction also indicated the bonding between iron and carbomethoxy groups of PCMCp^- .

The stronger inhibition effects of In and Fl than Cp are considered to be due to the action of benzene ring. As benzene and naphthalene showed weak inhibition effects, it is indisputable that the strong effects of In and Fl are mainly caused by the function of the cyclopentadiene ring. If In coordinates to an iron metal through the cyclopentadiene ring, the remained diene group in the benzene ring has possibilities to coordinate to another iron atom and/or to take polymerization reactions. Occurrence of polymerization reactions were suggested by the result that the inhibition efficiency of In increased with time more rapidly than Cp as shown in Fig. 5.

The dienes and trienes other than cyclopentadiene derivatives showed inhibition effects only on the cathodic reaction. It is likely that these compounds coordinated to an iron atom in the neutral η^4 -diene or η^6 -triene form and that the electron back-donation from the iron in the cathodic reaction to the π^* -orbital of the compounds stabilize the bonding between them. The inhibition efficiency of 1,3-COD decreased with time as shown in Fig. 5. The amount of 1,3-COD adsorbed on the iron surface corresponded to apparent thickness of about four molecular layers on the surface. The above results indicated that the polymerization of 1,3-COD was accelerated on the iron surface and that the product showed little inhibition effect due to the lack of any strong bonding site with iron such as cyclopentadiene ring in the case of indene.

5. Conclusion

In the cyclic dienes and trienes, cyclopentadiene derivatives showed strong inhibition effects on the iron corrosion in sulfuric acid even at a low concentration of 10^{-6} M . The polarization curve of the iron electrode inhibited with Cp indicated the formation of iron- η^5 -cyclopentadienyl bond on the surface. The higher inhibition efficiency of In than Cp was considered to be caused by the polymerization reaction of the diene group in the benzene ring. A cyclopentadiene derivative, $\text{Na}^+\text{PCMCp}^-$, inhibited only the anodic reaction at higher concentrations than 10^{-2} M , indicating the bonding with iron through carbomethoxy groups. Polymerization reaction of 1,3-COD on the surface resulted in a decrease of the inhibition effect. It

is concluded that the π -bonding force of cyclic dienes and trienes with iron plays the most important role in the corrosion inhibition and that cyclopentadiene derivatives are most effective probably because of their ability to form stable metal- η^5 -cyclopentadienyl bonds.

(Received April 26, 1985)

References

- 1) F. Zucchi, G. L. Zucchini & G. Trabanelli: "Proceedings 3rd European Symposium on Corrosion Inhibitors", p. 121, Università Deglistude di Ferrara, Ferrara (1971).
- 2) S. B. Balenzin, N. I. Podobayev, A. G. Voskresensky & V. V. Vasiliyev: "Proceedings 3rd International Congress on Metallic Corrosion", Vol. 2, p. 9, Swetz-Zeitlingen, Amsterdam (1969).
- 3) J. N. Poutilova: "Comptes Rendus 2ème Symposium Européen sur 'les Inhibiteurs de Corrosion'", p. 139, Università Deglistude di Ferrara, Ferrara (1966).
- 4) G. L. Foster, B. D. Oakes & C. H. Kucera: *Ind. Eng. Chem.*, **51**, 825 (1969).
- 5) G. W. Poling: *J. Electrochem. Soc.*, **114**, 1209 (1969).
- 6) K. Aramaki & M. Ichimura: *Boshoku Gijutsu*, **29**, 437 (1980).
- 7) H. Uhlig: *Ind. Eng. Chem.*, **32**, 1490 (1940).
- 8) K. E. Heusler & G. H. Cartledge: *J. Electrochem. Soc.*, **108**, 732 (1961).
- 9) P. L. Timms: *J. Chem. Soc., Chem. Commun.*, 1033 (1969).
- 10) A. Z. Rubezhov, A. S. Ivanov & A. A. Berkukova: *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1606 (1979).
- 11) B. F. Hallam & P. L. Pauson: *J. Chem. Soc.*, 3030 (1956).
- 12) H. W. Sternberg & I. Wender: *Chem. Soc. Spec. Publ.*, **13**, 35 (1959).
- 13) R. B. King & A. Fronzaglia: *J. Chem. Soc., Chem. Commun.*, 547 (1965).
- 14) S. A. Keppie & M. F. Lappert: *J. Chem. Soc., (A)*, 3216 (1971).
- 15) R. S. Threlkel & J. E. Bercaw: *J. Organometal. Chem.*, **136**, 1 (1967).
- 16) R. C. Cookson, J. B. Heustock, J. Hudec & B. R. D. Whitear: *J. Chem., Soc., (C)*, 1986 (1967).
- 17) F. G. Bordwell & M. J. Bausch: *J. Am. Chem. Soc.*, **105**, 6188 (1983).
- 18) H. Nishihara & K. Aramaki: *Boshoku Gijutsu*, **33**, 493 (1984).
- 19) M. I. Bruce, J. K. Walton, B. W. Skelton & A. H. White: *J. Chem. Soc., Dalton Trans.*, 2227 (1982).