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Novel Surface Reaction of Iron. Growth of Crystalline $[FeX(OCOR)]_n$ ($X = Cl, Br, I$; $R = C_6H_5, C_6H_5CH{=}CH, C_6H_5CH_2$) on Surfaces of Iron and Stainless Steel Plates in Reactions with Mixtures of Carboxylic Acids (RCOOH) and Organic Halides (R′X)

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The reaction of metallic iron with carboxylic acids (RCOOH) in an aqueous solution is well known. However, only a little is known concerning the reaction of metallic iron with a mixture of RCOOH and organic halide under anhydrous conditions. Recently a number of chemical processes dealing with reaction systems containing carboxylic acid and organic halide (*e.g.*, synthesis of CH_3COOH from CH_3OH and CO by $Rh–CH_3I$ catalyst (Monsanto process [1]) and homologation of CH_3COOH by CO and H_2 using $Ru–CH_3COI$ catalyst (Texaco process [2])) have been developed. Therefore revealing the chemistry of the corrosion reaction of iron and stainless steel, which are used as materials of reaction vessels of the chemical processes, by the mixture of carboxylic acid and organic halide has become very important.

Recently we have found that crystals of $[FeX(OCOR)]_n$ grow on surfaces of iron and stainless steel plates when the plates are treated with mixtures of certain carboxylic acids (RCOOH) and organic halides (R′X). We now report the isolation and characterization of the iron compound.

When an iron (99.9%) plate (40 mm × 20 mm × 0.50 mm, 3.1 g, 56 mmol) was treated with a mixture of C_6H_5COOH (3.3 g, 27 mmol) and C_2H_5Br (2.9 g, 27 mmol) at 200 °C for 10 h in a glass autoclave under anhydrous conditions, 300 mg (1.2 mmol as the monomer unit) of yellowish brown crystals (usually flakes) of $[FeBr(OCOC_6H_5)]_n$ *1* were formed on the surface of the iron plate. The crystals were scraped up from the iron plate and washed by acetone repeatedly to obtain analytically pure *1*. Analytical data of *1* and its analogues are listed in Table I. The crystals of *1* were formed under a wide range of reaction conditions (molar ratio of C_6H_5COOH to C_2H_5Br = 0.5–3; temperature = 150–250 °C). However, use of C_6H_5COOH and C_2H_5Br separately in the reaction with iron caused no apparent corrosion.

The formation of *1* was accompanied by evolution of equimolar amounts of H_2 and $C_6H_5COOC_2H_5$, indicating that the corrosion reaction is expressed by the following equation:

$$Fe + 2C_6H_5COOH + C_2H_5Br \rightarrow (1/n)\,\mathit{1} + H_2 + C_6H_5COOC_2H_5 \qquad (1)$$

When *1* was treated with bpy (2,2′-bipyridine) in THF, $[Fe(bpy)_3]Br_2$ [3] and $Fe(OCOC_6H_5)_2$ were formed; the latter compound was isolated as a known 1:1 adduct of $Fe(OCOC_6H_5)_2$ and hydrazide of 4-pyridinecarboxylic acid [4].

TABLE I. Properties and Analytical Data of $[FeX(OCOR)]_n$.

Compound	Color	D.p.[a] (°C)	μ_{eff} (B.M.)	Analytical Data[b]		
				C	H	X
1	brownish yellow	425	4.82	32.5 (32.7)	1.9 (2.0)	31.4 (31.1)
2	pale brown	435	4.98	40.0 (39.6)	2.5 (2.4)	16.9 (16.7)
3	deep green	390	4.99	27.4 (27.7)	1.4 (1.6)	42.9 (42.7)
4	light yellow	388	5.15	37.7 (38.2)	2.4 (2.5)	27.5 (28.2)
5	pink	250	5.26	35.1 (35.5)	2.7 (2.6)	30.4 (29.5)

[a] Decomposition point determined by TGA. [b] Calculated values in parentheses.

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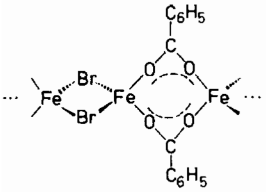
The difference between wave numbers of $\nu(COO)_{asym}$ (1540 cm^{-1}) and $\nu(COO)_{sym}$ (1380 cm^{-1}) in an IR spectrum of *1* suggests that the $OCOC_6H_5$ ligand serves as a bridging carboxylato ligand [5]. The high spin character of *1* with μ_{eff} value of 5.01 ± 0.04 B.M. not only supports that Fe in *1* is divalent but also suggests a tetrahedral structure around Fe. It is known that several tetrahedral iron compounds such as $[FeX_4]^{2-}$ show high spin states with the μ_{eff} values of *ca.* 5 [6]. Based on the IR and magnetic data of *1*, as well as the very low solubility of *1* in usual organic and inorganic solvents, we propose a polymeric structure shown below having the bridging $OCOC_6H_5$ and Br ligands,



Powder X-ray diffraction (X-ray = CuK_α) of *1* shows sharp diffraction peaks at 2θ = 12.3° (relative peak strength = 100), 18.5° (16), 24.8° (4), 31.2° (5), and 37.6° (7).

Other alkyl bromides in combination with C_6H_5COOH at 200 °C also gave *1* with evolution of H_2 and the corresponding ester. Use of $(CH_3)_3CCl$ and C_2H_5I in similar reactions gave $[FeCl(OCOC_6H_5)]_n$ *2* and $[FeI(OCOC_6H_5)]_n$ *3*, respectively. When $C_6H_5CH{=}CHCOOH$ and $C_6H_5CH_2COOH$ were employed in combination with C_2H_5Br, the reaction gave $[FeBr(OCOCH{=}CHC_6H_5)]_n$ *4* and $[FeBr(OCOCH_2C_6H_5)]_n$ *5*, respectively. Compounds *2–5* grow as flakes or needles on the surface of the iron plate, and their properties and IR and powder X-ray diffraction data suggest that they have similar structures to that of *1*.

Employment of stainless steel plate in the reaction with the mixture of C_6H_5COOH and R′X gave the same iron compound $[FeX(OCOC_6H_5)]_n$ as proved by IR and powder X-ray diffraction spectra. When SUS 304 stainless steel containing 18 wt.% of Cr and 8% of Ni was used, the rate of the reaction was about 60% of the rate of the reaction of iron. Increase in Cr and/or Ni content led to some decrease in the reaction rate, but the extent of the decrease was small indicating that Cr and Ni form no stable passive film in the reaction with the mixture of RCOOH and R′X. On the contrary, use of SUS 316 containing 2–3% of Mo besides Cr and Ni and SUS 321 containing *ca.* 1% of Ti showed strong inhibition effects of Mo and Ti against the corrosion. It is known that Mo-containing stainless steel has high resistance against corrosion by inorganic halogen compounds which usually cause corrosion of other stainless steels.

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