

## Reaction of Organic Halogen Compounds with Metals (Part I) A Formation of Organometallic Complex in Dimethyl Formamide Solvent

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### 有機할로겐 化合物과 金屬과의 反應 (第 1 報)

디메틸포름아마이드 溶媒存在下에서의 有機金屬복합체 生成에 關한 研究

金 裕 善\*

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#### Abstract

Reaction of organic chlorine containing ester, alcohol, and acids with metallic tin and zinc in dimethyl formamide solvent gave a good yield of organo metallic complex. The same reaction under a mixed U.V. irradiation could not give an appreciable yield of the complex except in the case of an elevated reaction temperature. The solvation effect of dimethyl formamide of the metallic complex formation was markedly increased as compared to the reaction in toluene and cyclohexane. In case of chlorine containing carboxylic acid, the formation of organo chloro zinc complex of the salt was observed. The reaction of organo zinc complex with a carbonyl precursor gave the addition product together with a dimerized product. Especially the aldehyde species enhanced the formation of zinc complex. The addition reaction was simple and convenient, but the yield was not high. (30-40% for the acid, 73% for the ester, 14.6% for alcohol). The result was discussed on basis of solvent effect and the procedures were described.

#### 要 約

有機할로겐 에스테르, 알콜, 및 酸과 金屬亞鉛 및 錫을 dimethyl formamide 溶媒存在下에서 反應시킨 結果 有機金屬 복합체를 좋은 收率로 生成하였다. 같은 反應을 混合紫外線照射下에서 進行시킨 結果 高溫 以外에서는 복합체의 生成이 크지못하였다. D.M.F. 에 依한 金屬 복합체의 溶解効果는 톨루엔이나 사이크로헥산보다 훨씬 컸었다. 鹽酸을 含有한 酸에서는 酸의 金屬鹽의 金屬 복합체가 生成됨을 觀察하였다. 카보닐 precursor 와의 反應에 있어서는 少量의 双化合物과 함께 附加物을 生成하였으나 收率이 높지 못하였다(酸 30-40%, 에스테르 73%, 알콜 14.6%). 그러나 이 方法은 從來法에 比하여 簡便한 것임을 알았다. 研究結果를 溶媒効果에 關聯시켜 論議하였으며 實驗方式을 報告하였다.

#### Introduction

Numerous reports have been appeared in the recent publications concerning on the formation and reactivity of the complex.<sup>1,2,3)</sup> The enhancement of the reactivity of the formation of the complex by the solvating effect of solvents was already observed by Kornblum<sup>4)</sup> and further obser-

vation concerning on the solvent effect of the reaction promotion and reaction intermediate solvating was reported by other workers<sup>5,6,7,8)</sup>. Their observations stated that the organo metallic reaction intermediates were solvated by a particular solvent which subsequently assists or enhances the reaction path. In some cases the reaction was remarkededly promoted by the application of solvent<sup>4)</sup>. The same observation was also reported

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in case of a free radical reaction by Walling<sup>9</sup>. The organo halogen zinc complex, the wellknown Reformasky reaction intermediate, was studied classically by many workers<sup>10</sup>, and the procedures were already established by many workers. However, the modification of the procedure and solvent consideration for the intermediate organo metallic complex solvating was not much investigated. The chlorine containing precursor was only known to be the least reactive one for the reaction. Various tin halogen complex were studied by various workers<sup>11</sup> and proved to form a dimerized product instead of the organo metallics in presence of toluene as the solvent for a reactive chlorine compounds. However, the solvation of the intermediate was not considered. Present interest based on the recent development of the solvation theory of the reaction intermediate was therefore concerned to the study for the promotion or enhancement of the reaction of compounds, especially the least reactive chlorine species, by the application of a particular solvent such as dimethyl formamide, dimethyl sulfoxide, and etc. Chlorine containing carboxylic acids, esters, and alcohols were chosen and the degree of the solvent effect of the formation of organometallic complex was studied. The primary result for the determination of the solvent effect will be extended to the reaction study of the intermediate formed in a particular solvent such as dimethyl formamide. The addition reaction of the organo zinc complex with a carbonyl precursor, which is the Reformasky reaction, might be interesting to be subjected to a close investigation, if the solvation of the intermediate can change the normal reaction sequence. A comparative study for the formation of the complex under various irradiation conditions by the application of particular solvent may be interesting to understand the mode of the solvent effect in a radical reaction. Present investigation therefore covers the primary study for the determination of the reactivity of the organo chlorine compounds in dimethyl formamide, toluene, and others, and the reaction study of the organo zinc chlorine complex with benzaldehyde and

acetophenone in the same solvent.

### Experimental\*

#### Starting Materials

Chloro acids (Fisher certified), Ethylene chlorohydrin (Fisher  $n_D^{25}$  1.4381,  $D_4^{25}$  1.1181), Dimethyl formamide (Merck and Wako Chemical b. pt. 151-53°  $n_D^{25}$  1.4260,  $D_4^{25}$  0.942) Cyclohexane, Toluene (Fisher) Benzaldehyde (Wako Chemical  $n_D^{25}$  1.5408,  $D_4^{25}$  1.012), and Acetophenone (Fisher  $n_D^{25}$  1.5305,  $D_4^{25}$  1.039) were obtained from commercial sources as indicated. The metallic Zinc powder (Merck) and Tin powder (Merck) were used without further processing. Ethyl monochloro acetate (b. pt. 143-45°,  $n_D^{25}$  1.4227) was prepared by the standard procedure. 1,2-Dichloro-3-phenyl propionic acid (m.p. 163-4°) was prepared by a photochlorination of cinnamic acid in carbon disulfide<sup>12</sup>. A Hanue Made Quartz High Pressure Immersion Lamp PL-313, Q-81 (Out put 70 W) was used as the irradiation source.

#### Identification of the products.

The products involved in this experimental are all known compounds. Therefore the products were identified by means of physical constants, qualitative tests, gas chromatography, and infrared spectrophotometry. The recovery of the starting materials in the later part of this experimental was measured using an integrator disc mounted on a Bristol recorder by means of gas chromatography.

**Standard procedures of the reaction of organic halogen containing acids, esters, and alcohol with zinc in dimethyl formamide and toluene.**

Into a 100 ml. round bottomed three necked flask equipped with a stirrer, condenser, and thermometer were placed 0.1 mole of metallic zinc powder, and 50.00 cc of the solvent and the mixture was refluxed under vigorous stirring. From a neck of the flask 0.1 mole of the halogen compounds was added in a several portions to the boiling mixture. The

\* The infrared spectra and gas chromatography were taken at this institute by means of Beckman IR-4 and GC-2 model, respectively. All melting points and boiling points were not corrected. The melting points were measured using a Fisher-Johns melting point stand.

reaction mixture was then refluxed under vigorous stirring during the course of 3-8 hours. The reaction mixture was filtered and the inorganic solid mass was extracted with acetone by means of a Soxhlet extractor in order to remove stannic chloride and other organics. The residue from the extraction, the recovered tin, was dried and weighed. The filtrate from the filtration of the reaction mixture and the acetone extracts were distilled, respectively, and the residue from the both distillations was combined together. The residue was distilled under reduced pressure in case of liquid products after acidification and extraction with

ether, or was crystallized in case of solid product. The product was identified by means of gas chromatography and infrared spectrophotometry. In some reaction run the filtrate was condensed to a small volume and acidified with 20% sulfuric acid solution. The aqueous solution was extracted with ether and the ether extracts were dried and distilled. The residue from the ether distillation was subjected to further purification. The results which was concerned to the determination of the reactivity of the compounds with metals in the solvents are summarized in the Table 1.

Table 1. Reactivity of organic halogen acids, esters and alcohol with tin.

Reactant	Amount g.	Metal	Amount g.	Solvent	Reaction time hrs	Unreacted tin g.	Reactivity %	Remarks Product
CH <sub>2</sub> ClCOOCH <sub>3</sub>	11.0	Sn	12.0	Toluene	8	11.0	8.3	(a)
ClCH <sub>2</sub> CH <sub>2</sub> OH	8.1	Sn	12.0	Toluene	3	10.1	11.7	(b)
C <sub>3</sub> F <sub>7</sub> COOH	13.5	Sn	6.5	D.M.F	3	5.0	20.3	(c)
CH <sub>2</sub> ClCOOH	9.4	Sn	12.0	Toluene	3	5.7	52.5	(d)
CH <sub>3</sub> ClCHCOOH	11.0	Sn	12.0	Toluene	3	9.4	24.4	(e)
CH <sub>3</sub> ClCHCOOH	19.0	Sn	12.0	Xylene	4.5	8.2	31.7	(f)
CH <sub>3</sub> ClCHCOOH	19.0	Sn	12.0	D.M.F.	4	7.4	38.3	(g)
C <sub>6</sub> H <sub>5</sub> CHClCHClCOOH	17.0	Sn	12.0	Toluene	8	4.6	61.7	(h)

(a) The unreacted ester was recovered. (d) The unreacted alcohol was recovered. (c) The acid salt was obtained. (d) 2.3 g. of the acid salt and 1.7 g. of the acid was obtained. (e) 1.1 g. of the acid salt and 2.9 g. of a tar was obtained. (f) 3.0 g. of the acid salt was obtained. No appreciable yield of the dimerized product. (g) From the acidified reaction mixture 4.4 g of the inorganic zinc salt was obtained. Anal. Calc. for ZnO, Calcd Zn:79.9 Found: 75.8% (h) The unreacted acid was recovered. 3.1 g. of cinnamic acid m. p. 133° was obtained. There were tarry mass which was the decomposition product.(3.2 g.)

**Standard procedures of the reaction of organic chlorine containing acids, fluoroacid, ester, and alcohol with zinc in toluene and dimethyl formamide.**

The same procedures described in the previous experiment (see above reaction) was adapted except few modifications. The reaction mixture was filtered and the inorganic mass filtered was triturated with water, dried, and weighed. The filtrate was acidified with dilute hydrochloric acid and the solution was divided into two parts. The first aliquot was continuously extracted with ether and the ether extract was dried and distilled. The ether, distillation residue was examined further or purified. The identification was based on the qualitative examination, infrared spectrophotometry, and gas chromatography. The second aliquot was neutralized with 5% solution of potassium hydroxide to give inorganic

zinc salt and zinc chloride. The solid was triturated with water, dried, weighed, and analyzed by radio activation.\*

The filtrate from the zinc salt separation was acidified again and the solution was extracted with ether. The ether solution was distilled and the residue was examined or purified further. The results which was mainly concerned to the determination of the reactivity of the compounds were summarized in the Table 2.

\* The author indebted for generous cooperation to Dr. Pijk and Mr. J.I. Kim at this Institute. The analysis was conducted by neutron activation of zinc and by comparing Zn<sup>65m</sup> with standard by means of RCL-256 channel analyzer. The chemical process of the irradiated sample was not conducted and a non-destructive method was adapted.

Table 2. Reactivity of organic halogen acids, esters, and alcohol with zinc in toluene and dimethyl formamide.

Reactant	Amount g.	metal	Amount g.	Solvent	Reaction time hr.	Unreacted zinc recovered g.	Reactivity %	Remarks
C <sub>3</sub> F <sub>7</sub> COOH	13.5	Zn	3.3	D.M.F.	3	1.7	50.0	(a)
ClCH <sub>2</sub> COOH	27.0	Zn	19.5	Toluene	4	3.8	80.5	(b)
ClCH <sub>2</sub> COOH	9.0	Zn	6.5	D.M.F.	4	0.4	93.5	(c)
ClCH <sub>2</sub> COOH	27.0	Zn	19.5	D.M.F.	4	2.4(d)	87.7	(e)
CH <sub>3</sub> CHClCOOH	17.0	Zn	10.9	D.M.F.	4	no residue(g)	100.0	(f)
ClCH <sub>2</sub> COOH	13.0	Zn	6.5	Toluene	4	17.0	—	(h)
ClCH <sub>2</sub> CH <sub>2</sub> OH	16.2	Zn	13.0	D.M.F.	4	7.2	44.6	(i)
ClCH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	24.0	Zn	13.0	D.M.F.	6	17.4(j)	—	(k)
ClCH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	12.0	Zn	6.5	D.M.F.	4	2.4(n)	63.1	(l)
ClCH <sub>2</sub> COOCH <sub>3</sub>	22.0	Zn	13.0	D.M.F.	4	5.4(ZnO)	100.0	(m)

(a) The acid salt was obtained. (b) Inorganic zinc salt [Zn(OH)<sub>2</sub> 5.6 g] from the alkaline solution. (c) (h) (l) The product analysis was reported in a separate reaction run in the later part of this experimental. (d) The reactivity was variable depending on the reaction temperature. This run was carried out at 150-140°. (e) The same to the (c). A polymerized tar 3.5 g. and salt 0.8 g. From the gas chromatographic analysis using a Carbowax 166-a 6' column propionic acid was identified. There were trace amount of the dimerized acid. (g) The surface of the solid was covered with a viscous oil, which was difficult to remove without decomposition. (i) 9.2 g of zinc salt Anal. calc. Zn for ZnO, calcd.: 79.9 found: 76.5 (j) The solid was covered with zinc oxide. (m) 7.4 g. of zinc salt was obtained Anal. Calc. Zn for Zn(OH)<sub>2</sub> calcd.: 65.0 found Zn 61.5 (n) Anal. calc. Zn for ZnO calcd.: 79.9 found: 77.6.

**Standard procedures for the reaction of organo chlorine containing acids, with tin and zinc under irradiation.**

Into a pyrex irradiation tube previously described<sup>(13)</sup> were placed the organic halogen acids, solvent, and metal powder. The reaction mixture was irradiated with external cooling during the course of 6-8 hours. The reaction mixture was filtered and

the filtered inorganic mass, mainly recovered metal, was triturated with water, dried, and weighed. The filtrate was distilled and the residue was examined directly, or was acidified, extracted with ether, and the ether distillation residue was examined.

Results which were mainly concerned to the reactivity study of the compounds were summarized in the Table 3.

Table 3. Photoreaction of organic halogen compounds with zinc and tin in dimethyl formamide and toluene.

Reactant	Amount g.	Metal	Amount g.	Solvent	Irradiation time hr.	Temp. °C	Recovery of metal g.
ClCH <sub>2</sub> COOH	9.5	Sn	6.0	Cyclohexane	8	60	0.9(a)
o-Cl-C <sub>6</sub> H <sub>4</sub> COOH	9.0	//	6.0	Cyclohexane	8	60	5.3(b)
CH <sub>3</sub> ClCHCOOH	21.0	//	6.0	Cyclohexane	8	60	5.7(c)
CH <sub>3</sub> ClCHCOOH	21.8	//	6.0	D.M.F.	7	0	all reacted (d)
CHClCHCOOH	21.8	//	6.0	Benzene	6	0	none reactivity (e)

(a) 3.9 g of the salt and 0.5 g. of the acid were obtained. (b) 8.0 g of the acid was recovered. The dimerized product was 0.5 g. (c) The acid was recovered. (d) The salt of the acid and the dimerized product (1 g.) m.p. 210°. (e) The acid was recovered.

**Reaction of monochloroacetic acid with zinc in dimethyl formamide.**

Into a 100 ml. three necked round bottomed flask, equipped with a stirrer, condenser, cooler, and a side arm addition funnel, were placed 6.5 g.(0.1 mol) of zinc in 50.00 cc of dimethyl formamide and

the mixture was stirred vigorously under reflux. Through the side arm addition funnel a stream of nitrogen, washed once with pyrogallol solution and concentrated sulfuric acid, was passed into the reaction system. When the reaction mixture reached the reflux temperature of the solvent, 9.5 g.

(0.1 mol) of the acid dissolved in 10.00 cc of the solvent was added in one portion to the boiling mixture. The mixture was then refluxed under vigorous stirring during the course of hours. The reaction mixture was cooled and the inorganic mass was filtered. The mass was mainly the recovered zinc amounted less than 0.1 g. From the filtrate the solvent was distilled off under reduced pressure and the residue, syrupy paste, was treated with 20.00% sulfuric acid solution, and the aqueous solution was extracted with ether. The ether extract was dried over anhydrous calcium chloride and the ether was distilled off. From the ether distillation a brownish residue was obtained. (1.5 g.,  $n_D^{20}$  1.3915) The gas chromatographic analysis indicated that the residue was mainly the acetic acid. Further extraction of the aqueous solution by other than batch extraction was not attempted. In a separate reaction run conducted in the same procedure as the present one, the distillation residue of the filtrate was acidified with dilute solution of hydrochloric acid and the solution was divided into two parts. The first aliquot was continuously extracted with ether and the ether extract was distilled. The residue from the ether distillation, a brownish oil was obtained, which was composed of zinc chloride, acetic acid, and trace of the dimerized acid, and 0.8 g. of the salt identified by physical and spectrophotometrical examination. The second aliquot was treated with 5% solution of potassium hydroxide solution and the precipitated solid was filtered, washed with water, and weighed after drying. The amount was 2.8 g. The analysis revealed it was zinc hydroxide. The filtrate was further acidified and extracted with ether, and the ether solution was dried and distilled. The residue from the ether distillation gave a trace quantity of yellowish solid, which was the dimerized acid identified by infrared spectrophotometry.

**Reaction of monochloroacetic acid, benzaldehyde, zinc, in dimethyl formamide.**

The apparatus and procedure for the previous reaction described above was adapted in this reaction except few modifications. Into the flask were placed 9.5 g. (0.15 mol) of zinc in 50 cc. of dimethyl

formamide. The reaction mixture was stirred vigorously under reflux. Through the addition funnel 9.5 g. (0.1 mol) of the acid dissolved in dimethyl formamide were added in one portion to the boiling mixture. After vigorous reaction was ceased (15 minutes) 11.0 g. (0.1 mol) of benzaldehyde was added to the reaction mixture during the course of 10 minutes and the reaction mixture was refluxed for 6 hours. The reaction mixture was cooled and the inorganic solid mass was filtered, and the filtrate was distilled under reduced pressure to give a brownish syrupy residue. The residue was 20% acidified with solution of sulfuric acid and the aqueous solution was extracted twice with ether. The ether solution was dried over anhydrous calcium chloride and distilled. From the ether distillation a brownish viscous tar was obtained. (6.7 g.) The tarry material was difficult to be distilled because of decomposition. It was therefore washed with 5% sodium hydroxide solution and the insoluble residue was triturated with alcohol to give the hydroxy acid, which was not crystallized. (a racemic mixture). From the alkaline washing the acid salt amounted 0.5 g. was obtained. (I.R. for the acid. Characteristic frequency 3490, 1690, 1280, 1240, 700  $\text{cm}^{-1}$ ). The acid weighed 5.5 g. was 38.1% of the theoretical value. The aqueous solution from the acid washing was distilled under reduced pressure to give 12.3 g. of zinc sulfate. (51.04%) The residue of the distillation was not treated further. In a separate reaction run the recovery of the acid was measured by gas chromatography. From the distillation residue, upon standing, a trace quantity of the acid, melting 190–191°, succinic acid, was obtained.

**procedure b.**

The same reaction was repeated in a medium scale reaction run. 20.0 g. of the acid, 22 g. of benzaldehyde, and 20.0 g. of zinc were reacted using 150 cc of dimethyl formamide. The reaction mixture after refluxing for four hours the inorganic material was filtered off and the residue from the distillation of the filtrate was extracted three times with ether. The ether extracts was washed with 5% aqueous alkaline solution and once with water.

The alkaline washing was acidified and the solution was extracted with ether. The ether solution was dried and distilled to give a brownish oil (1.0 g.  $n_D^{20}$  1.4145) which composed of mainly acetic acid examined by gas chromatography. The ether solution from the alkaline washing was distilled to give the following fractions b.pt. 91-2°/8 mm ( $n_D^{20}$  1.5225, 1.0 g.), 126-24°/8 mm ( $n_D^{20}$  1.5278, 0.5 g.) and a high boiling residue (135-7°/7 mm.). The residue was crystallized to give a yellowish solid (m.p. 113-5°, 0.5 g.) and viscous tar. (2.2 g.). The infrared spectra indicated that the formation of the hydroxy acid. The aqueous solution was further condensed to a small volume to give a solid (27.0 g. zinc sulfate). The concentrate was further distilled to dryness and triturated with water to give 3.3 g of yellowish oil and a crystal melted at 128-33°. The identification of the oil and crystal revealed that they were a mixture of cinnamic acid and the salt. From the solvent distillate and the aqueous distillate total 9.5 g. of benzaldehyde and 4.8 g. of acetic acid were obtained by gas chromatographic technique. The yield of the reaction was 42.5% of acetic acid, 19.3% of cinnamic acid (crude), 11.6% of hydroxy acid (crude), 43.9% of benzaldehyde, and of zinc sulfate. The material balance was not 100.00% because of decomposition.

#### Reaction of monochloroacetic acid, acetophenone and zinc in dimethyl formamide.

The same procedure for the reaction of benzaldehyde was adapted in this reaction run 9.5 g. (0.1 mole), 10.0 g. of zinc (0.15 mole), and 11.0 g. of benzaldehyde (0.1 mole) were reacted. From the separation procedure described above total 11.3 g. of zinc sulfate (66.8%), 7.8 g. to acetophenone (65.0%), and 0.8 g. of the hydroxy acid melting 110-113° (I.R. 3600, 1690, 1410, 1260, 1280, 690,  $cm^{-1}$ ) was obtained. The recovery of the aliphatic acid was not checked in this reaction run.

#### Reaction of ethylene chlorohydrine with zinc in dimethyl formamide.

The same procedures and separation scheme for the aldehyde reaction was followed in this reaction run. 8.0 g. of ethylene chlorohydrin (0.1 mole), 6.5 g. (0.1 mole) of zinc were reacted in 50.00cc of dime-

thyl formamide. From the reaction 5.5 g. of zinc (84.6%) were only recovered. The gas chromatographic following of the reaction product was not achieved. There were trace amount of ethylene glycol, but it was not consistent.

#### Reaction of ethylene chlorohydrine, benzaldehyde, zinc and dimethyl formamide.

The same procedures and separation scheme for the aldehyde was adapted in the present reaction run. 16.0 g. of chlorohydrin (0.2 mole), 22.0 g. of benzaldehyde (0.2 mole) and 13.0 g. of zinc (0.2 mole) were reacted in 100 cc of dimethyl formamide. From the reaction 4.8 g. of zinc (21.6%) was recovered. From the processing of the reaction mixture 7.3 g. of benzaldehyde (33.1%), zinc chloride, 3.2 g. of the diol boiling 190-93°/6 mm (a syrupy paste. I.R. 3600, 3000, 2880, 1200, 1100, 1065, 1030, 755, 700  $cm^{-1}$ ) (14.6%) were obtained. There was 1.5 g. of fraction boiling at 121°/8 mm. which was composed of the aldehyde and high boiling alcohol (ethylene glycol), examined by gas chromatography using 1.5' apiezon column, and an unidentified aromatics melting at 115-120° (0.2 g.)

#### Reaction of ethyl monochloroacetate, zinc, and dimethyl formamide.

The same procedures for the aldehyde reaction run of the acid was adapted in this reaction run. 12.0 g. (0.1 mol) of the ester, 6.5 g. (0.1 mol) of zinc in 50.00 cc of dimethyl formamide was reacted as previously. From the reaction 2.4 g. (36.9%) of zinc was recovered. There were no other product except the recovery of the unreacted ester. Because of the separation scheme adapted the amount of the recovery of the ester was not measured. There were at trace quantity of the diethyl succinate which was examined by gas chromatographic technique.

#### Reaction of ethyl monochloroacetate, benzaldehyde, zinc, and dimethyl formamide.

The procedures and separating scheme for the reaction of aldehyde and acid were adapted for the present reaction run. 24.0 g. of the ester (0.2 mole), 13.0 g. (0.2 mole) of zinc, and 22.0 g. of benzaldehyde (0.2 mole) were reacted in 150 cc of dimethyl formamide as previously. From the reaction 4.2 g.

of zinc(32.3%) was recovered. From the triturating the filtrate of the reaction mixture 12.3 g. (55.9%) of benzaldehyde, 5.4 g. of ethyl cinnamate boiling 148-52/12 mm. (33.1%) (I.R. 3050, 1740, 1650, 1330,

1205, 990, 870, 760, 710  $\text{cm}^{-1}$ ). There were 6.9 g. (43.0%) of a polymerized tar which was composed of ethyl cinnamate unit identified by infrared spectrophotometry.

Table 4. A modified Reformasky reaction of organic chlorine containing acid, ester, and alcohol in dimethyl formamide.

Reactant	Amount mol.	Carbonyl compounds	Reaction time hr.	Reaction temp. °C	Zinc recovered %	Product	
						Organic %	Inorganic %
$\text{ClCH}_2\text{COOH}$	0.1	$\text{C}_6\text{H}_5\text{CHO}$	6	Reflux	—*	0.5 g of Salt Crude acid 38.1%	$\text{ZnSO}_4$ 51.04
$\text{ClCH}_2\text{COOH}$	0.2	$\text{C}_6\text{H}_5\text{CHO}$	4	Reflux	—*	HOAc 42.5% Cinnamic acid 19.3 Hydroxy acid 11.6 Aldehyde(recovered) 43.6	$\text{ZnSO}_4$ 56.0
$\text{ClCH}_2\text{COOC}_2\text{H}_5$	0.2	$\text{C}_6\text{H}_5\text{CHO}$	4	Reflux	32.3	Aldehyde recovered 55.9 Ethyl cinnamate 33.1 Polymer 43.0	
$\text{ClCH}_2\text{CH}_2\text{OH}$	0.2	$\text{C}_6\text{H}_5\text{CHO}$	4	Reflux	21.6	Diol 14.6% Aldehyde recovered 33.1 Trace glycol	
$\text{ClCH}_2\text{COOC}_2\text{H}_5$	0.1	$\text{C}_6\text{H}_5\text{COCH}_3$	4	Reflux	—*	Acetophenone recovered 65.0 Acid(hydroxy) 0.5 g	$\text{ZnSO}_4$ 66.8

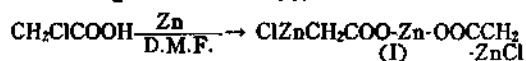
\* The inorganic solid mass obtained from the reaction was composed of Zn and zinc salt which was difficult to separate without decomposing zinc.

### Results and Discussion

The organic chlorine containing compounds, the least reactive species of the corresponding halogen compounds, reacted with tin and zinc in toluene and dimethylformamide, as summarized in the Table 1, and 2. The product composition of the reaction was rather complicated because of the partial decomposition of the intermediate complex. Therefore the reactivity was mainly considered in the present research. The product was composed of unreacted acid, salt, the decomposition product of the complex and inorganic salt. In few cases such as acid and ester the trace quantity of the dimerized product was observed. The relative reactivity of the chlorine in each series with metal increased as the reactivity of the chlorine atom in the molecule is increased as expected, even though an extensive case was not studied because of the defect of material supply. The reactivity was also depend on the reaction temperature and solvent. The temperature effect was rather insignificant as compared to the solvent effect. However, the change of solvent from the toluene, known to be inert, to

the dimethyl formamide resulted in the increase of reactivity. Especially zinc complex was formed almost quantitative rate in case of acid and ester within a short reaction period. In each reaction run carried out in toluene solvent, there obtained a syrupy paste which was hydrolyzed with water to zinc salt, but the same reaction in dimethyl formamide solvent did not give any apparent insoluble residue on the metallic surface. This observation was lead to the concept of solvation effect of the solvent in the formation of metallic complex. The effect of solvent in the reaction and the solvation of a reaction intermediate are known for some times for the Ullmann reaction by Kornblum<sup>1)</sup>, and dimethyl formamide was one of the strong solvating solvent according to their observation. The recent publication by E. Desey et al.<sup>2)</sup> stated that the solvating effect of the reaction intermediate was significant enough to alter the structural influence of the molecule on the reaction path. The same observation was reported by Walling et al.<sup>3)</sup> for a free radical intermediate. For the polarity of solvent Delarmare et al.<sup>4)</sup> reported to alter reaction path of a nucleophilic substitution

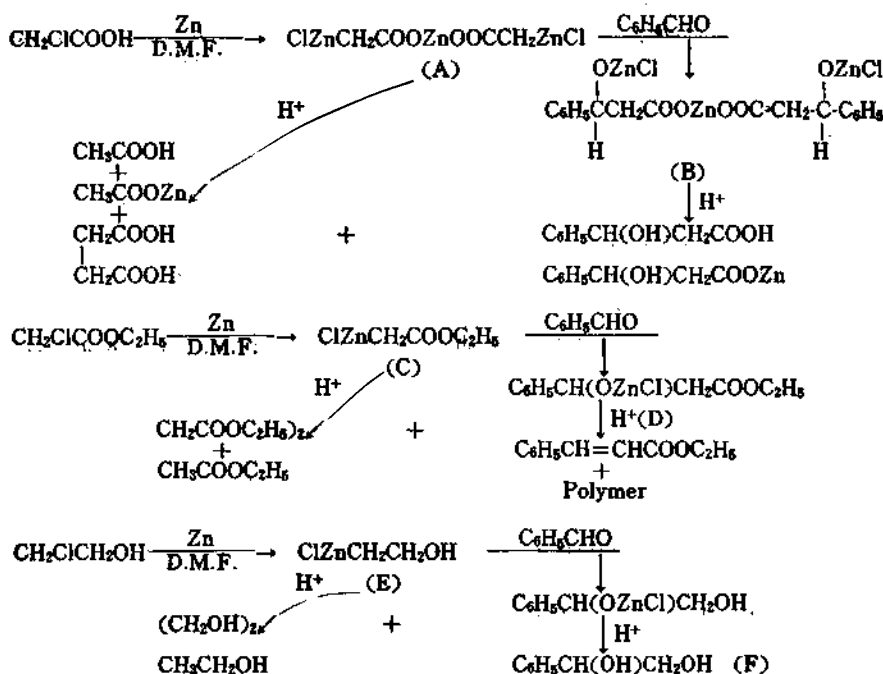
and it had been quite extensively studied. For an organic complex the formation does not involve any significant character of nucleophilic substitution and the intermediate ionic concept for the Wurtz type reaction was replaced by the free radical intermediate. Therefore the present observation was due to solvating the organic metallic complex formed in dimethyl formamide. Further extension of the study was made, therefore, to ascertain the solvent effect by trapping the formed complex with a carbonyl precursor such as benzaldehyde and acetophenone. (Table 4) In the reaction with acid series an interesting phenomenon was observed. When the equivalent quantity of the acid, zinc, and aldehyde was reacted, the reaction proceeded within a hour to dissolve all zinc whereas the same reaction without carbonyl precursor gave the unreacted zinc. The same procedure was followed by changing the reactant ratio to 1:1.5:1 of acid, zinc, and aldehyde. Surprisingly the reaction proceeded smoothly without any induction period to dissolve all zinc. The reaction was extended to an acetophenone system, but the reaction of acid in this case was not quantitative. However, the reactivity of the acid was exceeded than that of the reaction of the acid alone. These observation suggested also the following intermediate (I),



The formation of the acid salt in the present reaction condition was confirmed by reacting a fluoro carboxylic acid with zinc to give a 50.0% yield of the salt. Therefore the acid with chlorine will form not more than 50.0% of the salt. This point was further clarified by examining the reaction mixture of the trapping experiment. From the acid reaction 50-60% of zinc sulfate was obtained by condensing the acidified reaction mixture whereas the same reaction of the chloroacetate gave only zinc chloride without any zinc sulfate. In addition to this the reaction of acetophenone with acid gave a 60.0% yield of the zinc sulfate even though the yield of the addition product was trace and most of acetophenone was recovered. The formation of the intermediate (I) was, therefore, apparent. However, difficulties were encountered

in the separating the reaction product because of solubility of the acid and the water solubility of the solvent which made the physical separation difficult. This addition reaction, a modified Reformasky reaction, which involves rather insoluble salt complex, leads to the concept of the solvating the intermediate complex. Reformasky reaction, which have been extensively studied<sup>10)</sup>, requires an induction period, and a solvent. (toluene, benzene, ether, etc.) even for the reactive bromo precursor, and the chloro precursor was known to be the least reactive species. Present observation for a chlorine compounds indicated that the reaction did not require any induction period and reaction time was relatively short (1-4 hours) even for the chlorine precursor, which is the least reactive species. The conclusion was therefore drawn to have the solvating effect of dimethyl formamide for a Reformasky reaction intermediate of chlorine precursor. Probably the reaction proceeded to form the intermediate (I) for the acid and the solvent solvated the intermediate to give the reaction product within a short sequence. The chlorine compounds which were known to be least reactive for the Reformasky reaction was therefore a reactive species when the system applied a particular solvating solvent such as dimethyl formamide. The reaction procedure was studied further. The chlorohydrin gave 14.6% yield of the addition product together with a trace of dimerized product, and the chloroacetate gave a 33.1% of the unsaturated ester together with a high boiling polymerized ester (43.0%). In case of the acid the yield was 30% because of decomposition during separation. Even though the yield is relatively low and further investigation was warranted, the procedure was simple and convenient for an unreactive chlorine precursor, which will be better than existing procedure in case of high boiling aldehyde and of insoluble Reformasky reaction intermediate in the solvent such as toluene and etc. In conclusion the present observation results the following reaction path, in which the intermediate complex was remarkably solvated by the dimethyl formamide to promote the reaction.





The zinc intermediates of (A)(B)(C)(D)(E)(F) were all solvated by the dimethyl formamide.

In a separate reaction run the reactivity of chlorine containing acid were examined in order to ascertain the solvent effect under an irradiation condition. The solvent effect was also observed in the case of dimethyl formamide as compared to benzene in the case of reaction of tin with chloropropionic acid. (Table 3) Further investigation along this line will be reported in a separate paper.

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