

THE BROMINE-SbCl₅-CO-LIQ.SO₂ SYSTEM
 ELECTROPHILIC REACTION OF CHLORO-OXOCARBONIUM ION
 IN LIQUID SULPHUR DIOXIDE¹

by M. Yoshimura, T. Namba and N. Tokura

Department of Applied Chemistry, Faculty of Engineering,

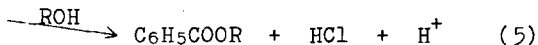
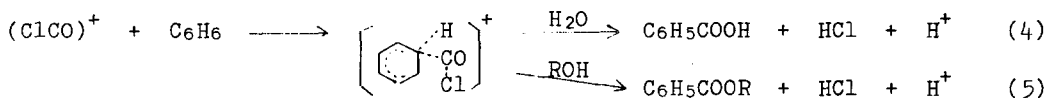
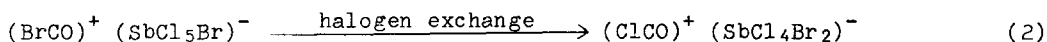
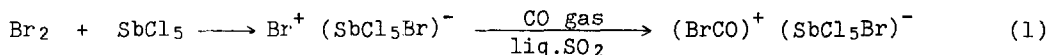
Osaka University, Suita, Osaka, Japan

(Received in Japan 2 April 1973; received in UK for publication 11 May 1973)

In the present communication we wish to report on the result of the electrophilic carbonylation by using Br₂-SbCl₅-liq.SO₂ system at -70°C to introduce -COOH or -COOR group into aromatic hydrocarbons and amines.

Carbon monoxide gas was bubbled into the solution consisting of bromine (0.05 mole), SbCl₅ (0.05 mole) and 50 ml of liq.SO₂ at -70°C for 1 hour while stirring. To this mixture 0.05 mole of a hydrocarbon or amine was dropped and stirred for more 1 hour. For the preparation of esters instead of acids 0.2 mole of ethanol was added into this mixture and stirred for more 30 min. The reaction mixture was poured into a large excess of chilled water, extracted with ether and treated further by ordinary procedures to obtain the carboxylic acids, carbamic acids or their ethyl esters.

The scheme will be written as the following:



The reaction involves the formation of bromo-oxocarbonium ion in liq. SO₂, followed by the halogen exchange to afford chloro-oxocarbonium ion as are indicated in eqs. (1) and (2).

The evidence for the presence of chloro-oxocarbonium ion as the intermediate comes from the formation of chloroformic acid ethyl ester, ClCOOC₂H₅, by the reaction, eq. (3). By use of a preparative gas-chromatography the reaction mixture gave chloroformic acid ethyl ester. Anal. Calcd. for C₃H₅O₂Cl : C, 33.20 ; H, 4.65. Found : C, 33.20 ; H, 4.73, Mass. m/e, 63 (ClCO)⁺, IR. (Neat), 1700 (formic acid ester), 1170-1130, 830 cm⁻¹.

Another evidence in favour of the presence of (ClCO)⁺ ion as the intermediate is obtained from the IR spectrum of the vapour of the reaction mixture, eq. (2). To this mixture dry nitrogen gas was introduced and the expelled gas was collected in a gas-cell and examined. The spectrum supports the presence of (ClCO)⁺. IR. (gas), 1827 (>CO) and 849 (C-Cl) cm⁻¹.

However the yield of benzoic acid from benzene appears to be low (31%), benzene (the starting material) is recovered as much as 58% and the overall yield for the reacted benzene goes up to 73.8%.

Table 1. Electrophilic Carbonylation of Aromatic Hydrocarbons and Various Amines in Br₂-SbCl₅-CO-liq. SO₂ System at -70°C: Ethyl Ester Formation.

Material	Product (yield %)
Benzene	C ₆ H ₅ COOC ₂ H ₅ (31), Benzene (recovered), (58)
Toluene	<u>o</u> -Toluic acid ethylester (8), <u>p</u> -Toluic acid ethylester (13) Halogenated toluenes, Monohalogenated (33) + Dihalogenated (35)
Cyclohexylamine	C ₆ H ₁₁ NHCOOC ₂ H ₅ (34), Cyclohexylamine (recovered), (60)
n-Hexylamine	<u>n</u> -C ₆ H ₁₃ NHCOOC ₂ H ₅ (37), <u>n</u> -Hexylamine (recovered), (62)
Diethylamine	(C ₂ H ₅) ₂ N-COOC ₂ H ₅ (77), Diethylamine (recovered), (20)

Reference :

1. Carbonylation in liq. SO₂, Part V. The preceding paper in this series, Part IV, M. Nojima, F. Shiba and N. Tokura, Chemistry Letters, 2, 1137 (1972).