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Influence of Protonation on Gattermann−Koch Formylation Rate of Alkylbenzene in $CF_3SO_3H-SbF_5$

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The influence of the protonation on Gattermann−Koch formylation rate of alkylbenzenes was studied in CF_3SO_3H-SbF_5. From the kinetic study of *m*-xylene formylation using various SbF_5:*m*-xylene molar ratios in CF_3SO_3H, it is revealed that the formylation rate is explained with the equations which take into account the protonation equilibrium of *m*-xylene, and the apparent formylation rate is decreased by the protonation. The decrease of the apparent formylation rate by the protonation is proportional to the ratio of protonated alkylbenzene to form the σ-complex; therefore, the apparent relative formylation rate of alkylbenzenes is not consistent with their relative basicity under strong acidic conditions such as in $CF_3SO_3H-SbF_5$.

Introduction

The reaction of aromatic compounds with CO to give aromatic aldehydes under acidic conditions is well-known as the Gattermann−Koch formylation,[1] and some reviews have been published.[2] The $HCl-AlCl_3$,[1,3] $HF-BF_3$,[4] and CF_3SO_3H[5] systems have all been investigated as formylation catalysts.

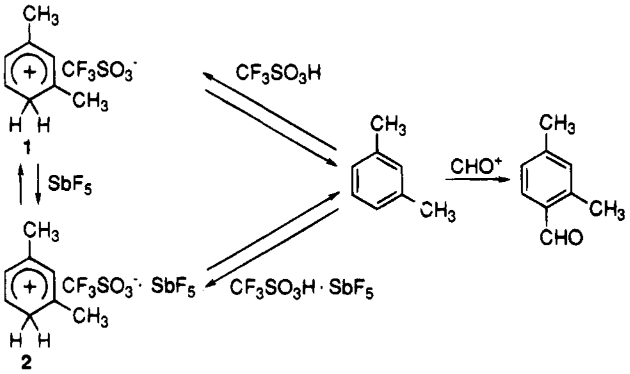
Recently, we reported that HSO_3F-SbF_5[6] and $HF-SbF_5$[7] are also useful catalyst systems for the Gattermann−Koch formylation. Although most aromatic compounds are formylated more quickly by increasing the SbF_5:substrate molar ratio in these systems, reactive aromatic compounds such as 1,3,5-trimethylbenzene and methylnaphthalenes are formylated more slowly. The protonation of reactive aromatic compounds to form the σ-complex (arenium ion complex) under strong acidic conditions seems to decrease the apparent formylation rate because of a reduction in the aromatic concentration. The Gattermann−Koch formylation has been reported as an electrophilic substitution using the formyl cation (CHO^+),[5b,8] and the protonation of aromatic compounds inhibits its rate as it inhibits nitration[9] and acylation.[10]

In this paper, we wish to report the influence of protonation on the formylation rate of alkylbenzenes in $CF_3SO_3H-SbF_5$.

Results and Discussion

In order to estimate the protonation ratio of an alkylbenzene in $CF_3SO_3H-SbF_5$, ^1H-NMR spectral measurements were obtained and formylation experiments of *m*-xylene were carried out using various SbF_5:*m*-xylene molar ratios in CF_3SO_3H. When *m*-xylene was added to CF_3SO_3H, one broad singlet peak of CF_3SO_3H and benzene ring protons were observed (Figure 1). Similar ^1H-NMR spectra were obtained in CF_3SO_3H-SbF_5 when the SbF_5:*m*-xylene molar ratio was less than 1. Under these conditions, the ^1H-NMR spectra show that there is a fast proton exchange between benzene ring protons and CF_3SO_3H, and a part of the *m*-xylene is protonated by CF_3SO_3H and $CF_3SO_3H{\cdot}SbF_5$ to form σ-complexes **1** and **2**, respectively (Scheme 1).[11]

Scheme 1



On the other hand, when the SbF_5:*m*-xylene molar ratio was greater than 1 (Figure 1), the ^1H-NMR spectra drastically changed and showed that most of the *m*-xylene was protonated to form σ-complex **2**.[12] This result indicates that $CF_3SO_3H{\cdot}SbF_5$ is a far stronger acid than CF_3SO_3H, and σ-complex **2** is more stable than σ-complex **1**. On the other hand, the yield of aldehyde showed a very interesting tendency depending on the SbF_5:*m*-xylene molar ratio (Figure 2). The formylation proceeded more slowly with an increase in the SbF_5:*m*-xylene molar ratio when the SbF_5:*m*-xylene molar ratio was less than 1. This result seems to reflect the increase in the σ-complex **2**, which is a more stable ion pair than **1**, and which does not react with the formyl cation because of charge repulsion.

On the contrary, the formylation proceeded more quickly with increasing SbF_5:*m*-xylene mole ratios under

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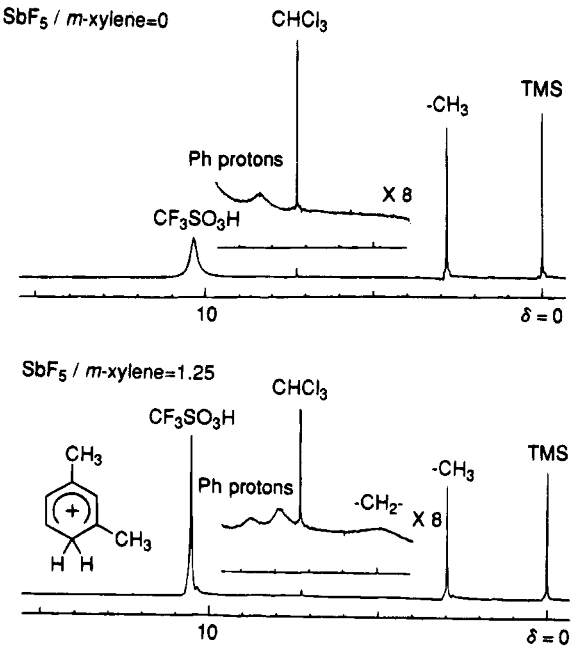

Figure 1. ^{1}H-NMR of *m*-xylene in $CF_3SO_3H-SbF_5$ at 0 °C.

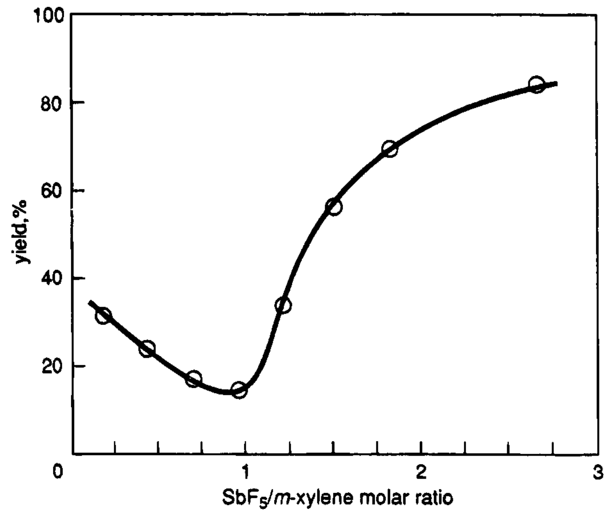

Figure 2. Apparent formylation rate of *m*-xylene in $CF_3SO_3H-SbF_5$. The reaction time was 1 h.

conditions where this ratio was greater than 1. Excess SbF_5, which does not protonate *m*-xylene, is considered to raise the formyl cation concentration and consequently increase the formylation rate.

In addition, the formylation of 1-methylnaphthalene-d_{10} was carried out in $HF-SbF_5$ at −78 or 0 °C, and the H−D ratio was measured by ^{1}H-NMR. There was no difference in the H−D ratio between the formyl group and the aromatic ring of the produced aldehyde at 0 °C. On the other hand, although formylation did not occur at all at −78 °C, part of the deuterium of the aromatic ring was exchanged for hydrogen. In a control experiment, the H−D exchange of the formyl group was not observed under the same conditions. From these results, it was shown that protonation occurs faster than formylation.

From these preliminary experimental results, we postulated that the formylation of *m*-xylene (ArH) in $CF_3SO_3H-SbF_5$ can be explained in two ways by considering the protonation equilibrium according to whether the SbF_5:*m*-xylene molar ratio is less than or greater than 1 (Scheme 2). K_{TfOH} and K_{COTf} represent the equilibrium constants for the protonation of ArH and CO by CF_3SO_3H, K_{SbF5} and K_{COSb} are the equilibrium constants for the protonation of ArH and CO by $CF_3SO_3H{\cdot}SbF_5$, and k and k' are the rate constants of the formylation by CF_3SO_3H and $CF_3SO_3H{\cdot}SbF_5$, respectively. In this scheme, while CF_3SO_3H has two roles, which are the protonation of *m*-xylene and the production of formyl cation, $CF_3SO_3H{\cdot}SbF_5$ acts only to protonate *m*-xylene under conditions where the SbF_5:*m*-xylene molar ratio is less than 1. On the other hand, $CF_3SO_3H{\cdot}SbF_5$ protonates *m*-xylene and produces the formyl cation, but CF_3SO_3H is just a solvent when the SbF_5:*m*-xylene molar ratio is larger than 1. The most important concept used here is that CF_3SO_3H and $CF_3SO_3H{\cdot}SbF_5$ are recognized as different species. $CF_3SO_3H{\cdot}SbF_5$, being a far stronger acid, allows us to consider the equilibrium constants K_{SbF5} and $K_{COSb} \gg K_{TfOH}$ and K_{COTf}. Therefore, the formylation rate can be explained in terms of $k[CHO^+CF_3SO_3^-][ArH]$ and $k'[CHO^+CF_3SO_3^-{\cdot}SbF_5][ArH]$, respectively.

Scheme 2

SbF_5 / *m*-xylene ≦ 1

$$ArH + CF_3SO_3H \rightleftharpoons ArH_2^+CF_3SO_3^-$$
$$ArH + CF_3SO_3H{\cdot}SbF_5 \longrightarrow ArH_2^+CF_3SO_3^-{\cdot}SbF_5$$
$$CO + CF_3SO_3H \rightleftharpoons CHO^+CF_3SO_3^-$$
$$ArH + CHO^+CF_3SO_3^- \longrightarrow ArCHO + CF_3SO_3H$$
$$K_{TfOH} = \frac{[ArH_2^+CF_3SO_3^-]}{[ArH][CF_3SO_3H]}$$
$$K_{COTf} = \frac{[CHO^+CF_3SO_3^-]}{[CO][CF_3SO_3H]}$$
$$\frac{d[ArCHO]}{dt} = k[CHO^+CF_3SO_3^-][ArH]$$

SbF_5 / *m*-xylene ≧ 1

$$ArH + CF_3SO_3H{\cdot}SbF_5 \rightleftharpoons ArH_2^+CF_3SO_3^-{\cdot}SbF_5$$
$$CO + CF_3SO_3H{\cdot}SbF_5 \rightleftharpoons CHO^+CF_3SO_3^-{\cdot}SbF_5$$
$$ArH + CHO^+CF_3SO_3^-{\cdot}SbF_5 \longrightarrow ArCHO + CF_3SO_3H{\cdot}SbF_5$$
$$K_{SbF5} = \frac{[ArH_2^+CF_3SO_3^-{\cdot}SbF_5]}{[ArH][CF_3SO_3H{\cdot}SbF_5]}$$
$$K_{COSb} = \frac{[CHO^+CF_3SO_3^-{\cdot}SbF_5]}{[CO][CF_3SO_3H{\cdot}SbF_5]}$$
$$\frac{d[ArCHO]}{dt} = k'[CHO^+CF_3SO_3^-{\cdot}SbF_5][ArH]$$

In order to determine K_{COTf} and K_{COSb}, the volume of CO absorbed by various compositions of $CF_3SO_3H-SbF_5$ was examined at 0 °C. However, the volume was dependent only on the amount of CF_3SO_3H (18 mL of CO gas per 1 mol of CF_3SO_3H liquid). Therefore, the concentration of formyl cation seems extremely low, and [CO] is considered as the initial value $[CO]_0$ in both systems. Our results are consistent with the fact that the formyl cation has not been observed in the liquid phase.[5b,13]

To determine the protonation equilibrium constants of *m*-xylene, K_{TfOH} and K_{SbF5}, the UV-vis spectra of solutions of *m*-xylene in $CF_3SO_3H-SbF_5$ were obtained. However, the molar extinction coefficient of protonated *m*-xylene

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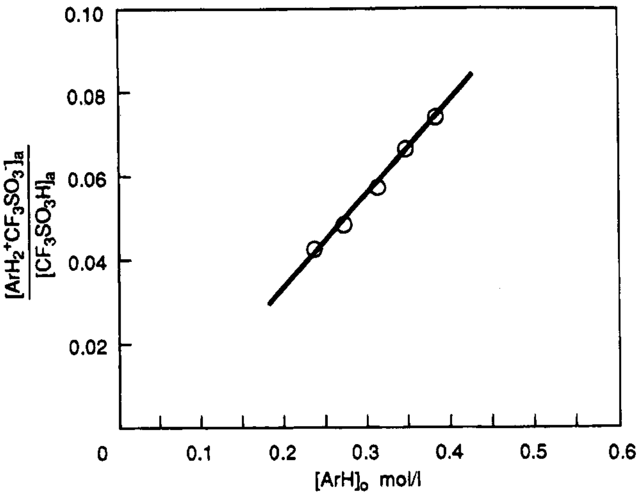
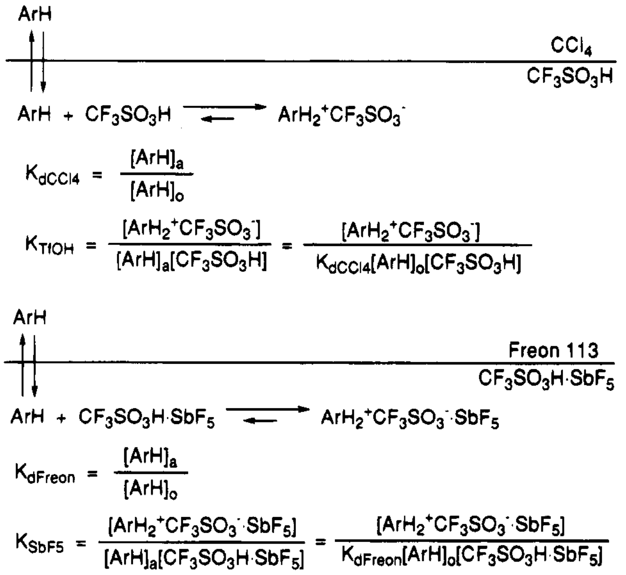


Figure 3. Correlation of $[ArH]_o$ with $[ArH_2^+CF_3SO_3^-]_a/[CF_3SO_3H]_a$. The amount of *m*-xylene was 6–10 mmol.

Scheme 3



was too large (more than 9000 L/mol) to allows us to measure the equilibrium in this way. Therefore, the equilibrium constants were estimated by an extraction method,[14] and *m*-xylene in the acid layer was presumed to be completely protonated under these conditions. CCl_4 and 1,1,2-trichlorotrifluoroethane (Freon 113) were chosen as the organic extraction solvents for CF_3SO_3H and $CF_3SO_3H{\cdot}SbF_5$, respectively, because they are sufficiently inert and insoluble (Scheme 3). In Scheme 3, K_{dCCl_4} and K_{dFreon} represent the distribution constants of *m*-xylene between CCl_4 or Freon 113 and the acid layer, and $[ArH]_o$ and $[ArH]_a$ represent the concentration of *m*-xylene in the organic and acid layers, respectively. The plots of $[ArH]_o$ versus $[ArH_2^+CF_3SO_3^-]/[CF_3SO_3H]$ and $[ArH_2^+CF_3SO_3^-{\cdot}SbF_5]/[CF_3SO_3H{\cdot}SbF_5]$ gave very good linear relationships as shown in Figures 3 and 4, respectively. From these figures, the values were estimated as 0.2 for $K_{dCCl_4}K_{TfOH}$ and 70 for $K_{dFreon}K_{SbF_5}$. The distribution constants of *m*-xylene, K_{dCCl_4} and K_{dFreon}, could not be determined because it was impossible to measure $[ArH]_a$; however, the distribution constants are smaller than 1 and do not seem to be very different from each other. The result is consistent with the fact that $CF_3SO_3H{\cdot}SbF_5$ is a far stronger acid than CF_3SO_3H.

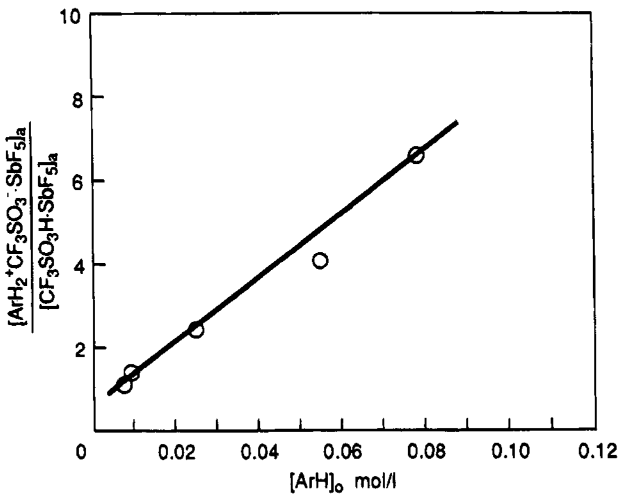


Figure 4. Correlation of $[ArH]_o$ with $[ArH_2^+CF_3SO_3^-{\cdot}SbF_5]_a/[CF_3SO_3H{\cdot}SbF_5]_a$. The amount of *m*-xylene was 5–9 mmol.

The kinetic study of *m*-xylene formylation was carried out based on its equilibria (Scheme 2), and the initial reaction rate method was employed because SbF_5 forms a complex with produced aldehyde that changes the solution composition. The formylation rate equations were converted by using the initial values where the subscript o means the initial concentration and $[CF_3SO_3H]$ is considered constant. The plots of $[ArCHO]/t$ versus $[CO]_o([ArH]_o - [CF_3SO_3H{\cdot}SbF_5]_o)$ gave an excellent linear relationship as shown in Figure 5 when the SbF_5: *m*-xylene molar ratio varied from 0 to 0.6. Similarly, the graphs of $[ArCHO]/t$ versus $[CO]_o[ArH]_o$ showed a good

SbF_5 / *m*-xylene ≤ 1

$$[ArH] + [ArH_2^+CF_3SO_3^-] + [ArH_2^+CF_3SO_3^-{\cdot}SbF_5] = [ArH]_o$$

$$[ArH_2^+CF_3SO_3^-{\cdot}SbF_5] = [CF_3SO_3H{\cdot}SbF_5]_o$$

$$[CO] = [CO]_o$$

$$[ArH] = \frac{[ArH]_o - [CF_3SO_3H{\cdot}SbF_5]_o}{K_{TfOH}[CF_3SO_3H] + 1}$$

$$[CHO^+CF_3SO_3^-] = K_{COTf}[CO]_o[CF_3SO_3H]$$

$$\frac{d[ArCHO]}{dt} = k[CHO^+CF_3SO_3^-][ArH] = \frac{kK_{COTf}[CF_3SO_3H]}{K_{TfOH}[CF_3SO_3H] + 1}[CO]_o([ArH]_o - [CF_3SO_3H{\cdot}SbF_5]_o)$$

SbF_5 / *m*-xylene ≥ 1

$$[ArH_2^+CF_3SO_3^-{\cdot}SbF_5] + [CF_3SO_3H{\cdot}SbF_5] = [CF_3SO_3H{\cdot}SbF_5]_o$$

$$[ArH] + [ArH_2^+CF_3SO_3^-{\cdot}SbF_5] = [ArH]_o$$

$$[CO] = [CO]_o$$

$$[ArH] = \frac{[ArH]_o}{K_{SbF_5}[CF_3SO_3H{\cdot}SbF_5] + 1}$$

$$K_{SbF_5}[CF_3SO_3H{\cdot}SbF_5] >> 1$$

$$[ArH] = \frac{[ArH]_o}{K_{SbF_5}[CF_3SO_3H{\cdot}SbF_5]}$$

$$[CF_3SO_3H{\cdot}SbF_5] = [CF_3SO_3H{\cdot}SbF_5]_o - [ArH]_o$$

$$[ArH] = \frac{[ArH]_o}{K_{SbF_5}([CF_3SO_3H{\cdot}SbF_5]_o - [ArH]_o)}$$

$$[CHO^+CF_3SO_3^-{\cdot}SbF_5] = K_{COSb}[CO]_o([CF_3SO_3H{\cdot}SbF_5]_o - [ArH]_o)$$

$$\frac{d[ArCHO]}{dt} = k'[CHO^+CF_3SO_3^-{\cdot}SbF_5][ArH] = \frac{k'K_{COSb}}{K_{SbF_5}}[CO]_o[ArH]_o$$

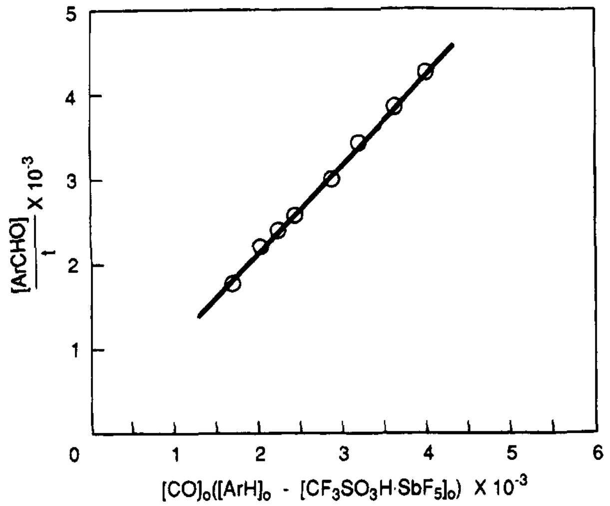


Figure 5. Correlation of $[CO]_0([ArH]_0 - [CF_3SO_3H{\cdot}SbF_5]_0)$ with $[ArCHO]/t$. The SbF_5:*m*-xylene molar ratio was 0−0.6, and the reaction time was 5 min.

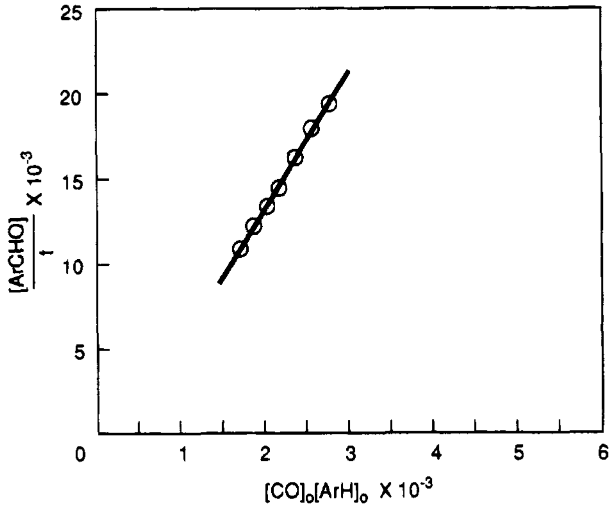


Figure 6. Correlation of $[CO]_0[ArH]_0$ with $[ArCHO]/t$. The SbF_5:*m*-xylene molar ratio was 7−19, and the reaction time was 1 min.

linear relationship as shown in Figure 6 under the conditions where the SbF_5:*m*-xylene molar ratio was from 7 to 19.

On the other hand, when the SbF_5:*m*-xylene molar ratio was from 2 to 4.5, it was found that the plots of $[ArCHO]/t$ versus $[CHO^+CF_3SO_3^-{\cdot}SbF_5]=[CO]_0([CF_3SO_3H{\cdot}SbF_5]_0 - [ArH]_0)$ had a good linear relationship as shown in Figure 7.

$$\frac{d[ArCHO]}{dt} = k'[CHO^+CF_3SO_3^-{\cdot}SbF_5] = k'K_{COSb}[CO]_0([CF_3SO_3H{\cdot}SbF_5]_0 - [ArH]_0)$$

This result is coincident with the suggestion from the result of the CO absorption experiment and shows that the formyl cation concentration is low enough to explain the formylation rate as a pseudo first order reaction, although the concentration of *m*-xylene is very low. For example, [ArH] is at most 6.8 mmol/L in a solution of *m*-xylene (10 mmol), CF_3SO_3H (100 mmol), and SbF_5 (30 mmol).

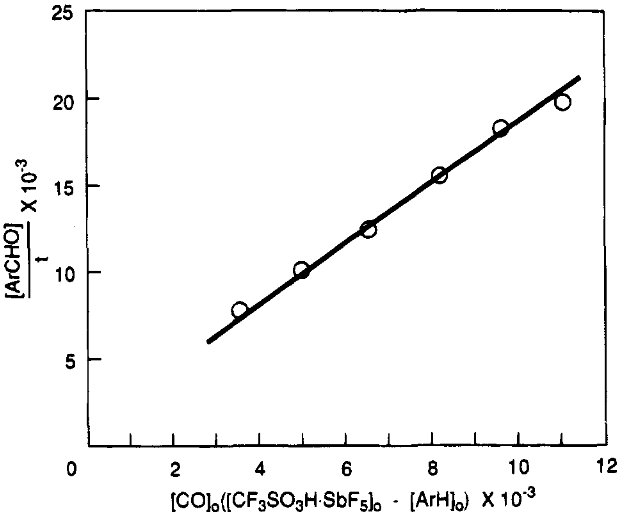


Figure 7. Correlation of $[CO]_0([CF_3SO_3H{\cdot}SbF_5]_0 - [ArH]_0)$ with $[ArCHO]/t$. The SbF_5:*m*-xylene molar ratio was 2−4.5, and the reaction time was 1 min.

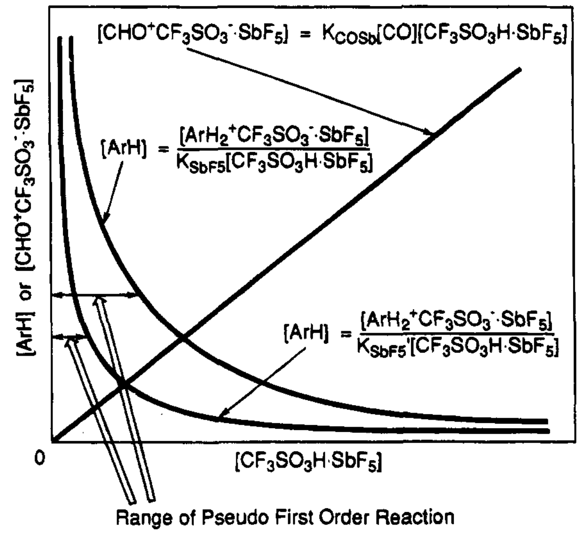


Figure 8. Correlation of $[CF_3SO_3H{\cdot}SbF_5]$ with [ArH] or $[CHO^+CF_3SO_3^-{\cdot}SbF_5]$ ($K_{SbF5} < K_{SbF5}'$).

When the SbF_5:*m*-xylene molar ratio is greater than 7, $CF_3SO_3H{\cdot}SbF_5$ decreases the concentration of *m*-xylene due to the protonation, and results in the formylation rate being seen as a second order reaction. Now, it is interesting that the formylation rate is explained as a second order reaction under these conditions although [ArH] was far greater under conditions when the SbF_5:*m*-xylene molar ratio is smaller than 1. The appearance of the pseudo first order reaction can be explained by considering that $CHO^+CF_3SO_3^-$ cannot directly react with alkylbenzene because $K_{COSb} \gg K_{COTf}$ when most of the *m*-xylene is protonated by $CF_3SO_3H{\cdot}SbF_5$.

$$ArH_2^+CF_3SO_3^-{\cdot}SbF_5 + CHO^+CF_3SO_3^- \longrightarrow$$
$$ArH + CHO^+CF_3SO_3^-{\cdot}SbF_5 + CF_3SO_3H \longrightarrow$$
$$ArCHO + CF_3SO_3H{\cdot}SbF_5 + CF_3SO_3H$$

The range of the pseudo first order reaction where [ArH] is far greater than $[CHO^+CF_3SO_3^-{\cdot}SbF_5]$ clearly decreases while increasing the value of the protonation equilibrium constant, K_{SbF5}, which is proportional to the basicity of a used alkylbenzene as shown in Figure 8. From these results, it seems that the apparent relative formylation rate is not proportional to the relative basicity under

Table 1. Apparent Relative Reactivity of 1,2,3-Trimethylbenzene with *m*-Xylene in CF_3SO_3H-SbF_5[a]

SbF_5:alkylbenzenes molar ratio	aldehyde yields (%) from 1,2,3-trimethylbenzene	aldehyde yields (%) from *m*-xylene	product ratio
0.1	18	18	1.0
0.35	16	18	0.9
0.6	12	16	0.8
0.85	9	14	0.6
1.1	10	11	0.9
1.35	24	22	1.1
1.85	44	41	1.1

[a] The reaction time was 30 min.

Scheme 4

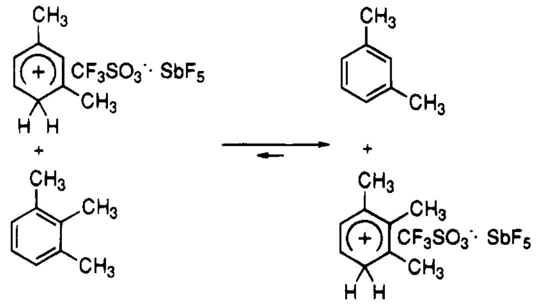


Table 2. Apparent Relative Reactivity of Alkylbenzene in CF_3SO_3H[a]

alkylbenzene	aldehyde yields (%) from alkylbenzene	aldehyde yields (%) from *m*-xylene	product ratio	relative basicity[b]
benzene	0	32	0.0	0.0035
toluene	0	35	0.0	0.024
p-xylene	4	40	0.1	0.038
o-xylene	18	45	0.4	0.042
m-xylene		38	1	1
1,2,4-trimethylbenzene	51	30	1.7	2.4
1,2,3-trimethylbenzene	35	30	1.2	2.7
1,2,4,5-tetramethylbenzene	0	24	0.0	5.4
1,2,3,4-tetramethylbenzene	35	24	1.5	15
1,3,5-trimethylbenzene	0	20	0.0	500
1,2,3,5-tetramethylbenzene	0	18	0.0	615

[a] The reaction time was 1 h. [b] The value was cited from ref 14.

conditions where the formylation rate is expressed as a second order reaction which involves the term [ArH] that is dependent on protonation. On the contrary, the apparent relative formylation rate is coincident with the relative basicity when the formylation rate is explained as a pseudo first order reaction.

The influence of protonation on the apparent relative formylation rate was studied by the competitive formylation of 1,2,3-trimethylbenzene and *m*-xylene at various SbF_5:alkylbenzene molar ratios in CF_3SO_3H. The results are summarized in Table 1. Although the reactivity of 1,2,3-trimethylbenzene is greater than that of *m*-xylene in electrophilic substitutions, the apparent formylation rate of *m*-xylene was greater than that of 1,2,3-trimethylbenzene in the presence of SbF_5 when the SbF_5:alkylbenzene molar ratio was less than 1. This result suggests that more 1,2,3-trimethylbenzene than *m*-xylene was protonated by $CF_3SO_3H{\cdot}SbF_5$ because the basicity of 1,2,3-trimethylbenzene is greater than that of *m*-xylene (Scheme 4).

The apparent relative formylation rate of various alkylbenzenes was compared with their relative basicities using *m*-xylene as a standard in CF_3SO_3H in the absence of SbF_5. The results are shown in Table 2. The relative basicity of the alkylbenzenes have been reported in several papers[14,15] and are listed in Table 2. The apparent relative formylation rate increased with an increase in the relative basicity in cases of benzene, toluene, and xylenes.

However, 1,2,4-trimethylbenzene showed the greatest apparent formylation rate, and the apparent relative formylation rate decreased with increasing basicity in the case of tri- and tetramethylbenzenes. These results suggest that the more basic alkylbenzenes are protonated more completely, and consequently their formylation is not proportional to their relative basicities.

In conclusion, the formylation rate of alkylbenzenes should be explained by considering their protonation equilibria. The extent of inhibition of the formylation by protonation is related to the extent of conversion to an inactive σ-complex, and therefore, the apparent relative formylation rate of alkylbenzenes is not generally proportional to their relative basicities. The results suggest that rates for normal Friedel–Crafts reactions like aromatic nitration[9] and acylation[10] where acidic conditions are employed have to take account of these equilibria.

Experimental Section

All aromatic starting materials, SbF_5 (Aldrich), CF_3SO_3H (Kishida Chemicals), and CO (Nippon Oxygen) were of the highest available purity and were used without further purification. CF_3SO_3H contained 5 mol % H_2O for Figure 6 and 7 and 1.5 mol % for others. H_2O was considered to be converted to $CF_3SO_3H{\cdot}H_2O$ or $SbF_5{\cdot}H_2O$ as an inert additive. A Yanagimoto G-3800 attached with a 1.5-m packed column (OV-17) or G-6800 attached with a 30-m capillary column (TC-1) gas chromatograph equipped with an on-line automatic integrator were used for GC analysis. MS analyses (GC-MS) were performed on a Hitachi M-2000 instrument fitted with a 30-m capillary column (TC-1). ^1H and ^{13}C-NMR spectra were recorded on a JEOL FX-200 (200 MHz) spectrophotometer. Infrared spectra were obtained on a JASCO IRA-1 instrument.

Formylation Procedures in CF_3SO_3H–SbF_5. A required amount of SbF_5 and CF_3SO_3H (200 mmol, 30 g) were put into a three-necked flask (300 mL) equipped with a CO gas buret under atmospheric pressure. *m*-Xylene (10 mmol, 1.06 g) or a mixture of alkylbenzene (10 mmol) with *m*-xylene (10 mmol, 1.06 g) was added into CF_3SO_3H–SbF_5 at a stretch with vigorous stirring at 0 °C. The reaction mixture was quenched in ice–water and extracted with benzene. In all experiments, unreacted substrates were recovered. The yields of products were determined by GC, and products were characterized by IR, ^1H-NMR, ^{13}C-NMR, and mass spectra analysis after the isolation by a vacuum distillation.

Formylation Procedures in HF–SbF_5. HF (500 mmol, 10 g) and SbF_5 (7.5 mmol, 1.63 g) were put into a Hastelloy Taiatsugarasu autoclave (100 mL) equipped with a Hastelloy magnetic stirrer bar with cooling at −78 (using dry ice–acetone bath) or 0 °C (using ice–water bath). The autoclave was sealed, and CO (20 atm) was introduced. Then, 1-methylnaphthalene-d_{10} (10 mmol, 1.52 g) was added through a syringe into the solution with vigorous stirring under temperature control. After the reaction was over, the autoclave was depressurized and opened with cooling below 0 °C. The reaction mixture was quenched in ice–water and extracted with benzene, and the H–D ratio for the formyl group and the aromatic ring of produced aldehyde was determined by ^1H-NMR after isolation.

Extraction Experiment Procedures. A required amount of *m*-xylene, CCl_4 (15 g), and CF_3SO_3H (100 mmol, 15 g) were put into an Erlenmeyer flask with a stopper (30 mL), and the

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[14] McCaulay, D. A.; Lien, A. P. *J. Am. Chem. Soc.* **1951**, *73*, 2013.
[15] Kilpatrick, M.; Luborsky, F. E. *J. Am. Chem. Soc.* **1953**, *75*, 577.

mixture was stirred vigorously at 0 °C. After the flask was settled for 3 h at 0 °C, the CCl_4 layer was separated and the concentration of *m*-xylene by GC was determined.

Similarly, *m*-xylene, 1,1,2-trichlorotrifluoroethane (15 g), CF_3SO_3H (10 mmol, 1.50 g), and SbF_5 (10 mmol, 2.17 g) were poured into the flask, and the 1,1,2-trichlorotrifluoroethane layer was separated after the flask was settled for 5 min.

Study of Carbon Monoxide Absorption into CF_3SO_3H–SbF_5 Procedures. A three-necked flask (300 mL) equipped a CO gas buret under atmospheric pressure, and a cylinder which contained a mixture of CF_3SO_3H (100 mmol, 15 g) and required amount of SbF_5 (0–30 mmol, 0–6.51 g) was immersed in an ice–water bath. Water was kept from getting in all equipments. The mixture was added into the flask through the cylinder, and the volume of CO absorption was determined with the gas buret.

^{1}H-NMR Study Procedures. All ^{1}H-NMR measurements were carried out at 0 °C using a coaxial system. A mixture of *m*-xylene (10 mmol, 1.06 g), SbF_5 (0–15 mmol), and CF_3SO_3H (200 mmol, 30 g) was put into a 5 mm inner glass tube, and $CDCl_3$ with TMS was added into a 10 mm outer glass tube.

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