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Dual Reactivity of the Formyl Cation as an Electrophile and a Brønsted Acid in Superacids

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The nature of the formyl cation in the Gattermann–Koch formylation was studied by comparing the formylation with the acetylation and sulfonation in $CF_3SO_3H-SbF_5$ and FSO_3H-SbF_5, respectively. The results of the kinetic studies in $CF_3SO_3H-SbF_5$ showed that the formyl cation has dual reactivity as an electrophile and as a Brønsted acid. Upon comparing the formylation with the sulfonation in FSO_3H-SbF_5, it was found that the protonated aromatic compounds also act as Brønsted acids to produce formyl cations. Therefore, the formylation has a priority over other typical electrophilic substitutions under conditions where most of aromatic compounds are protonated because the formyl cation is reproduced close to the aromatic compounds by the protonation of CO with not only superacids but also protonated aromatic compounds.

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] CF_3SO_3H,[5] FSO_3H-SbF_5,[6] and $HF-SbF_5$[7] systems were investigated as the formylation catalysts.

Recently, we reported that the protonation equilibrium of *m*-xylene (ArH) should be taken into account to determine the formylation rate in $CF_3SO_3H-SbF_5$.[8] In this work, the formylation rate showed three aspects which were one pseudo first order reaction ($k[CHO^+CF_3SO_3^-\cdot SbF_5]$) and two second order reactions ($k'[CHO^+CF_3SO_3^-][ArH]$ and $k[CHO^+CF_3SO_3^-\cdot SbF_5][ArH]$) which depend on the SbF_5/*m*-xylene molar ratio. The two second order reactions appeared when the SbF_5/*m*-xylene molar ratio was 0–0.6 and 7–19, respectively. On the other hand, the pseudo first order reaction was observed under conditions where the SbF_5/*m*-xylene molar ratio was 2–4.5. There is a question as to why $CHO^+CF_3SO_3^-$ does not react with *m*-xylene to produce the pseudo first order reaction under the conditions where most of the *m*-xylene was protonated by $CF_3SO_3H-SbF_5$, in other words, when the SbF_5/*m*-xylene molar ratio was greater than 1. As an answer for this question, we suggested that the $CF_3SO_3H-SbF_5$ that protonates the *m*-xylene acts as a stronger Brønsted acid than CF_3SO_3H to form $CHO^+CF_3SO_3^-\cdot SbF_5$ from $CHO^+CF_3SO_3^-$. This suggestion stimulated us to study whether the formyl cation can act as a Brønsted acid, because the formyl cation is another species which is produced by the protonation with superacids in this reaction.

$$
\begin{aligned}
&ArH_2^+CF_3SO_3^-\cdot SbF_5 + CHO^+CF_3SO_3^- \rightarrow \\
&\quad ArH + CHO^+CF_3SO_3^-\cdot SbF_5 + CF_3SO_3H \rightarrow \\
&\qquad ArCHO + CF_3SO_3H-SbF_5 + CF_3SO_3H
\end{aligned}
$$

In this paper, we report on the dual reactivity of the formyl cation, an electrophile and a Brønsted acid, by comparing it with the acetylation and sulfonation in $CF_3SO_3H-SbF_5$ and FSO_3H-SbF_5, respectively.

Results and Discussion

Formylation and Acetylation in $CF_3SO_3H-SbF_5$. In order to disclose the difference in nature of the formyl cation compared to typical electrophiles, kinetic studies of the formylation and the acetylation using *m*-xylene were completed in $CF_3SO_3H-SbF_5$ at 0 °C because the acetyl cation, CH_3CO^-, is a typical electrophile which seems not to act as a Brønsted acid under superacidic conditions. These experiments were conducted with two methods, which were the addition of *m*-xylene with $CF_3SO_3H-SbF_5$ (method A) and neat *m*-xylene (method B) into $CF_3SO_3H-SbF_5$ with CO or CH_3COF. The reaction rate equation for method A can be explained as an electrophilic substitution after the dispersion of *m*-xylene is attained in $CF_3SO_3H-SbF_5$. On the other hand, the reaction rate equation for method B is comprised of two terms which represent the electrophilic substitution in method A and another electrophilic substitution until the dispersion of *m*-xylene is attained in $CF_3SO_3H-SbF_5$. This occurs when the amount of acetylated *m*-xylene and the time during the attainment of the dispersion of *m*-xylene are small and short enough so the values of $[ArH]_0$ and t in methods A and B, respectively, could be considered the same. The latter term is presented as a competitive reaction of the electrophilic substitution and the protonation to *m*-xylene. If an electrophile has a Brønsted acid nature, it will act as a Brønsted acid to omit the latter term in method B. These equations were shown as follows.

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$$\begin{tikzcd}
\mathrm{ArH_o} \arrow[rr, "E^+", "-H^+"'] \arrow[d, "H^+"] & & \mathrm{ArE_B - ArE_A} \\
\mathrm{ArH_2^+} \arrow[r, shift left, "-H^+"] & \mathrm{ArH} \arrow[l, shift left, "H^+"] \arrow[r, "E^+", "-H^+"'] & \mathrm{ArE_A}
\end{tikzcd}$$

Method A:

$$\frac{\mathrm{d[ArE]_A}}{\mathrm{d}t} = k_{\mathrm{E}^+}[\mathrm{E}^+][\mathrm{ArH}]$$

Method B:

$$\frac{\mathrm{d[ArE]_B}}{\mathrm{d}t} = \frac{\mathrm{d[ArE]_A}}{\mathrm{d}t} + c\frac{[\mathrm{E}^+]_o[\mathrm{ArH}]_o}{[\mathrm{E}^+]_o + [\mathrm{CF_3SO_3H{-}SbF_5}]_o}$$

In these equations, c, [ArH], [E^+], $[ArE]_A$, and $[ArE]_B$ represent the coefficient of the competitive reaction between the electrophile and the proton and the concentration of m-xylene, the electrophile, the product in method A, and the product in method B, respectively. These equations were converted using the initial concentration values, which are denoted with the subscript o as in our previous paper.[8]

Method A:

$$\frac{\mathrm{d[ArE]_A}}{\mathrm{d}t} = k_{\mathrm{E}^+}[\mathrm{E}^+][\mathrm{ArH}] = \frac{k_{\mathrm{E}^+}}{K}\,\frac{[\mathrm{E}^+]_o[\mathrm{ArH}]_o}{[\mathrm{CF_3SO_3H{-}SbF_5}]_o - [\mathrm{ArH}]_o - [\mathrm{E}^+]_o}$$

Method B:

$$\frac{\mathrm{d[ArE]_B}}{\mathrm{d}t} - \frac{\mathrm{d[ArE]_A}}{\mathrm{d}t} = c\frac{[\mathrm{E}^+]_o[\mathrm{ArH}]_o}{[\mathrm{E}^+]_o + [\mathrm{CF_3SO_3H{-}SbF_5}]_o}$$

In these equations, K is the protonation equilibrium constant of m-xylene with $CF_3SO_3H-SbF_5$. The reaction was completed under conditions where the SbF_5/m-xylene molar ratio was 7–20 at 0 °C; therefore, the CH_3COF that was added as an acetylation reagent appeared to completely convert to CH_3CO^+ in $CF_3SO_3H-SbF_5$.[9] In the case of acetylation, the plots of $[ArCOCH_3]_A/t$ versus $[CH_3CO^+]_o[ArH]_o/([CF_3SO_3H-SbF_5]_o - [ArH]_o - [CH_3CO^+]_o)$ in method A gave a good linear relationship as shown Figure 1. Similarly, the graphs of $([ArCOCH_3]_B - [ArCOCH_3]_A)/t$ versus $[CH_3CO^+]_o[ArH]_o/([CH_3CO^+]_o + [CF_3SO_3H-SbF_5]_o)$ in method B also showed a good linear relationship as presented in Figure 2. These results clearly indicate that the acetyl cation acts as a typical electrophile because the acetylation proceeded until the dispersion of m-xylene was attained. On the contrary, the formylation rate was explained only with the equation in method A, regardless of the methods, and the plots of $[ArCHO]/t$ versus $[CO]_o[ArH]_o$ showed a good linear relationship as shown in Figure 3. In control experiments, the formylation and the acetylation were not reversible reactions under these conditions. Therefore, these results clearly show that the formylation did not proceed to omit the latter term of the equation in method B until the dispersion of m-xylene was attained and that the formyl cation acted as a Brønsted acid to protonate m-xylene. From the results of these kinetic studies, a question arose as to how the formylation proceeds in spite of the ability of the formyl cation as a strong Brønsted acid to protonate aromatic compounds.

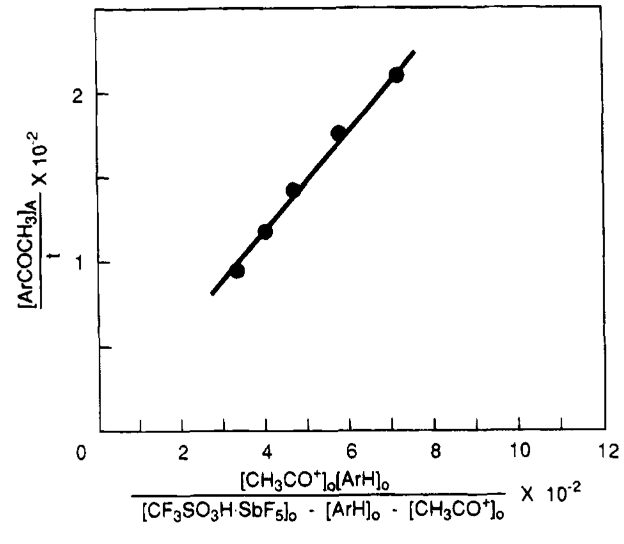
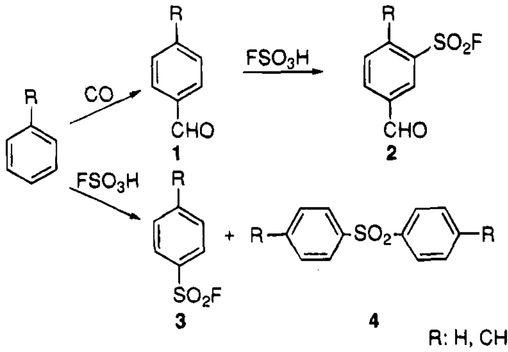


Figure 1. Correlation of $[CH_3CO^+]_o[ArH]_o/([CF_3SO_3H-SbF_5]_o - [ArH]_o - [CH_3CO^+]_o)$ with $[ArCOCH_3]_A/t$ (method A).

Formylation and Sulfonation in FSO_3H-SbF_5. In our previous work, it was found that both the formylation and the sulfonation take place to give four products from alkylbenzenes in the FSO_3H-SbF_5 system, and the ratio of these products depends on the ratio of FSO_3H and SbF_5.[6,10] In order to investigate whether the formyl cation acts as a Brønsted acid in FSO_3H-SbF_5, reactions of highly basic alkylbenzenes such as tri- and tetramethylbenzenes were carried out using various compositions of FSO_3H-SbF_5 under atmospheric CO pressure at 0 °C. When alkylbenzenes were slowly added into a mixture of FSO_3H and SbF_5 while being stirred vigorously, both the formylation and the sulfonation took place to give four compounds by a one-pot reaction, and this procedure is equal to method B. In this study, new compounds, formylalkylbenzenesulfonyl fluorides **2**, were obtained from 1,2,3-tri-, 1,3,5-tri-, and 1,2,3,4-tetramethylbenzene when the reaction time was prolonged.[6] The 1,2-shift of the methyl groups occurred, and this phenomenon was also observed in the Friedel–Crafts alkylations.[11] The results are summarized in Table 1. An unreacted



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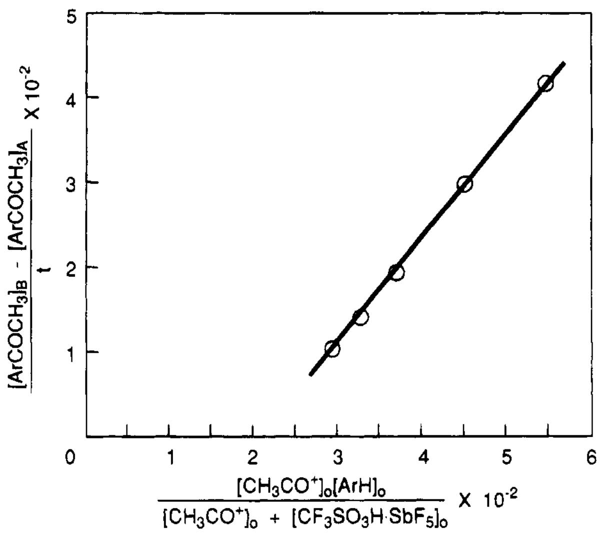

Figure 2. Correlation of $[CH_3CO^+]_o[ArH]_o/([CH_3CO^+]_o + [CF_3SO_3H-SbF_5]_o)$ with $([ArCOCH_3]_B - [ArCOCH_3]_A)/t$ (method B).

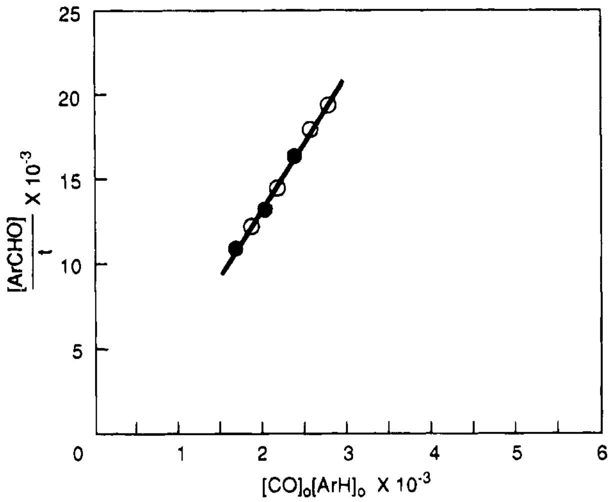

Figure 3. Correlation of $[CHO^+]_o[ArH]_o$ with $[ArCHO]/t$. ● and ○ represent the formylation by methods A and B, respectively.

Table 1. Formylation of Polyalkylbenzenes in FSO_3H-SbF_5[a]

alkylbenzene	SbF_5 (mmol)	product yields (%) 1	2	3	4
1,2,3-trimethylbenzene	13.8	12 (100:0)^c	0	32 (100:0)^c	0
	69.0	54 (89:11)^c	25^d	0	0
	138^b	60 (93:7)^c	11^d	3 (100:0)^c	0
1,2,4-trimethylbenzene	13.8	9^e	0	30^e	51 (91:9)^g
	69.0	90^e	1^f	0	0
	138	78^e	0	0	0
1,3,5-trimethylbenzene	13.8	0	0	80	0
	69.0^b	5	0	27	0
	138^b	9	0	13	0
1,2,3,4-tetramethylbenzene	13.8	12 (0:0:100)^h	0	33 (18:82)^i	0
	69.0^b	84 (11:7:82)^h	0	3 (100:0)^i	0
	138^b	67 (12:19:69)^h	0	1 (0:100)^i	0
1,2,3,5-tetramethylbenzene	13.8^b	0	0	76 (100:0)^i	0
	69.0^b	5 (18:82:0)^h	0	23 (94:6)^i	0
	138^b	1 (0:0:100)^h	0	2 (100:0)^i	0
1,2,4,5-tetramethylbenzene	13.8	4 (100:0:0)^h	0	87 (97:3)^i	0
	69.0^b	72 (97:0:3)^h	0	3 (100:0)^i	0
	138^b	75 (90:0:10)^h	0	1 (0:100)^i	0

[a] The reaction time was 1 h. [b] Unreacted alkylbenzene remained. [c] Isomer ratio of 2,3,4-trimethylbenzene derivative:2,4,5-trimethylbenzene derivative. [d] The yield of 5-formyl-2,3,4-trimethylbenzenesulfonyl fluoride. [e] Products were 2,4,5-trimethylbenzene derivatives. [f] The yield of 3-formyl-2,5,6-trimethylbenzenesulfonyl fluoride. [g] Isomer ratio of bis(2,4,5-trimethylphenyl) sulfone:2,4,5-trimethylphenyl 2,3,6-trimethylphenyl sulfone. [h] Isomer ratio of 2,3,5,6-tetramethylbenzaldehyde:2,3,4,6-tetramethylbenzaldehyde: 2,3,4,5-tetramethylbenzaldehyde. [i] Isomer ratio of 2,3,5,6-tetramethylbenzenesulfonyl fluoride and 2,3,4,6-tetramethylbenzenesulfonyl fluoride:2,3,4,5-tetramethylbenzenesulfonyl fluoride.

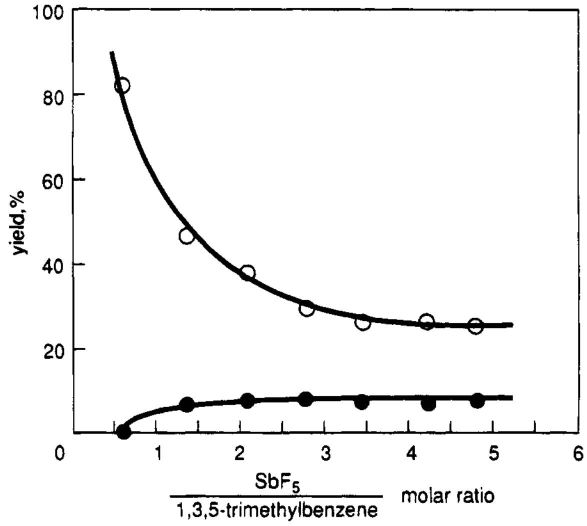

Figure 4. Reaction of 1,3,5-trimethylbenzene in FSO_3H-SbF_5. The reaction time was 1 h. ● and ○ represent the yields of formylated and sulfonated 1,3,5-trimethylbenzene, respectively.

substrate was recovered in some experiments, especially in the cases of 1,3,5-trimethylbenzene and 1,2,3,5-tetramethylbenzene. It was clear that this behavior was caused by the protonation, not by the steric hindrance of methyl groups, because the formylation of 1,2,4,5-tetramethylbenzene, which has a higher steric hindrance than 1,3,5-trimethylbenzene, quickly proceeded under the same conditions. When the amount of SbF_5 was small, the sulfonation was the main reaction. The formylation became predominant with the increase in SbF_5, except for 1,3,5-trimethylbenzene and 1,2,3,5-tetramethylbenzene. For these two compounds, the sulfonated compounds were the main products under all conditions. When the formylation of 1,3,5-trimethylbenzene was carried out using more various compositions of FSO_3H-SbF_5, the yield of sulfonated 1,3,5-trimethylbenzene decreased by the protonation with an increase in the SbF_5/1,3,5-trimethylbenzene molar ratio; however, that of the formylated 1,3,5-trimethylbenzene was almost constant as shown in Figure 4. These results reflect the fact that the formyl cation acts as a Brønsted acid more than as an electrophile for these highly basic aromatic compounds.

In order to clarify how to proceed with the formylation under conditions where most of the aromatic compounds are protonated, the time dependence of the product distribution from 1,3,5-tri- and 1,2,3,5-tetramethylbenzene was studied. The results are tabulated in Table 2, and the bis(alkylphenyl) sulfones **4** were not formed under these conditions. Although the yields of the sulfonyl fluorides **3** were constant, the yields of aldehydes

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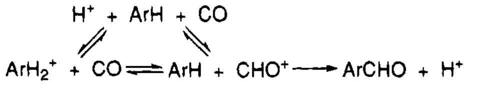
Table 2. Time Dependence of Product Distribution in FSO_3H-SbF_5[a]

alkylbenzene	time (h)	product yields (%)		
		1	**2**	**3**
1,3,5-trimethylbenzene	1	9 (100:0)[b]	0	13 (100:0)[b]
	2	15 (63:37)[b]	2 (100:0)[c]	14 (100:0)[b]
	4	17 (40:60)[b]	5 (100:0)[c]	9 (100:0)[b]
	8	26 (18:82)[b]	8 (100:0)[c]	9 (100:0)[b]
	24	37 (5:95)[b]	19 (92:8)[c]	10 (100:0)[b]
1,2,3,5-tetramethylbenzene	1	1 (0:0:100)[d]	0	2 (100:0)[f]
	2	3 (0:15:85)[d]	0	2 (100:0)[f]
	4	17 (0:20:80)[d]	0	1 (100:0)[f]
	8	48 (0:19:81)[d]	2[e]	3 (87:13)[f]
	24	41 (0:19:81)[d]	15[e]	2 (80:20)[f]

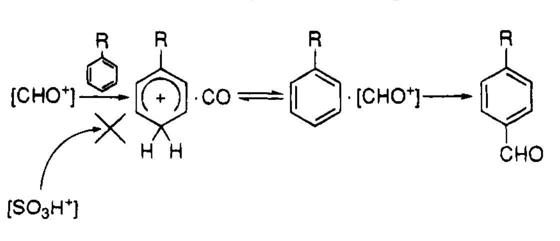
[a] The formylation was carried out using 138 mmol of SbF_5. Unreacted alkylbenzene was recovered in all experiments. [b] Isomer ratio of 2,4,6-trimethylbenzene derivative:2,4,5-trimethylbenzene derivative. [c] Isomer ratio of 3-formyl-2,4,6-trimethylbenzenesulfonyl fluoride:3-formyl-2,5,6-trimethylbenzenesulfonyl fluoride. [d] Isomer ratio of 2,3,5,6-tetramethylbenzaldehyde:2,3,4,6-tetramethylbenzaldehyde:2,3,4,5-tetramethylbenzaldehyde. [e] Product was 2-formyl-3,4,5,6-tetramethylbenzenesulfonyl fluoride. [f] Isomer ratio of 2,3,5,6-tetramethylbenzenesulfonyl fluoride and 2,3,4,6-tetramethylbenzenesulfonyl fluoride:2,3,4,5-tetramethylbenzenesulfonyl fluoride.

1 and **2** increased with time. In control experiments, the sulfonation and formylation were not reversible under these conditions. These results show that the formylation proceeded even after the alkylbenzenes were almost completely protonated, but the sulfonation took place only until the dispersion of alkylbenzenes was attained in FSO_3H-SbF_5. Because the formyl cation does not react with protonated aromatic compounds,[8] the formylation is clearly one of electrophilic substitutions. Therefore, the priority of the formylation over the sulfonation under strong acidic conditions, where most of the aromatic compounds are protonated, seems to be derived from the reproduction of the formyl cation closer to the aromatic compounds than to the other electrophiles by the protonation of CO with not only FSO_3H-SbF_5 but also protonated aromatic compounds in FSO_3H-SbF_5. This equilibrium among H^-, CO, and ArH is presented as follows.



$$ArH_2^+ + CO \rightleftharpoons ArH + CHO^+ \longrightarrow ArCHO + H^+$$

During the reproduction of the formyl cation, the reactive species for the sulfonation such as $[SO_3H^+]$[12] are unable to approach protonated aromatic compounds because of charge repulsion. This suggestion can give clear answers



to two questions about the formylation which are why the formylation of anisole proceeds using a weaker acid, $HF-BF_3$, instead of $HF-SbF_5$, which is the strongest superacid,[6,13] and why the formylation of the polynuclear aromatic compounds such as naphthalene and biphenyl does not occur in FSO_3H-SbF_5.[6,7] The answer for the former is that the formyl cation, $CHO^+SbF_6^-$, acts as a stronger Brønsted acid than $CHO^+BF_4^-$ to protonate anisole, and anisole is too basic to reproduce the formyl cation. The answer for the latter is that the formyl cation acts as a Brønsted acid for polynuclear aromatic compounds; however, the polyprotonation of the polynuclear aromatic compounds is difficult because of their charge repulsion, and the sulfonation takes place at the unprotonated aromatic ring to give sulfonated compounds as the main products.

In conclusion, it was found that the formyl cation has dual reactivity, as an electrophile and as a Brønsted acid, and protonated aromatic compounds also act as a Brønsted acid to produce formyl cations. Therefore, the formylation has the priority over other typical electrophilic substitutions under conditions where most aromatic compounds are protonated because the formyl cation is reproduced close to the aromatic compounds by the protonation of CO with not only superacids but also protonated aromatic compounds.

Experimental Section

All aromatic starting materials, FSO_3H (Morita Kagaku), SbF_5 (Aldrich), CF_3SO_3H (Kanto Kagaku), and CO (Nippon Sanso) were of the highest available purity and were used without further purification. The CF_3SO_3H contained 5 mol % of H_2O, which was considered to be converted to $SbF-H_2O$ as an inert additive. A Yanagimoto G-3800 or G-6800 gas chromatograph equipped with an on-line automatic integrator was used for GC analysis. A 30 m capillary column (TC-1) was used in the isomer separation, whereas a 1.5 m packed column (OV-17) was used in the yield determination. The MS analyses (GC−MS) were performed on a Hitachi M-2000 instrument fitted with a 30 m capillary column (TC-1). The ^1H-NMR spectra were recorded on a Hitachi R-24B (60 MHz) or a JEOL FX-200 (200 MHz) spectrophotometer, and the ^{13}C-NMR spectra were recorded on a JEOL FX-200 (50 MHz) spectrophotometer. The infrared spectra were obtained on a JASCO IRA-1 instrument.

Acetylation Procedures of Method A in $CF_3SO_3H-SbF_5$. A required amount of SbF_5, CF_3SO_3H (92 mmol, 13.82 g), and CH_3COF (20 mmol, 1.24 g) were put into a 300 mL three-necked flask at 0 °C. A solution of *m*-xylene (10 mmol, 1.06 g), a required amount of SbF_5, and CF_3SO_3H (108 mmol, 16.18 g) were added into the flask and stirred vigorously at 0 °C. The amounts of SbF_5 in the solutions in the flask and the added solutions were controlled so both solutions would be considered to have the same SbF_5 concentrations, taking into account the consumption of SbF_5 to protonate *m*-xylene and to produce CH_3CO^+. After 0.5 min, the reaction was quenched in ice−water, the mixture was extracted with benzene, and the product yields were determined using GC with an internal standard.

Acetylation Procedures of Method B in $CF_3SO_3H-SbF_5$. A required amount of SbF_5, CF_3SO_3H (200 mmol, 30.00 g), and CH_3COF (20 mmol, 1.24 g) were put into a 300 mL three-necked flask at 0 °C. *m*-Xylene (10 mmol, 1.06 g) was added into the flask and the mixture stirred vigorously at 0 °C. After 0.5 min, the reaction was quenched in ice−water and the mixture extracted with benzene, and the product yields were determined using GC with an internal standard.

Formylation Procedures of Method A in $CF_3SO_3H-SbF_5$. A required amount of SbF_5 and CF_3SO_3H (110 mmol, 16.60 g) were put into a 300 mL three-necked flask equipped with a CO gas buret under atmospheric pressure at 0 °C. A solution of *m*-xylene (10 mmol, 1.06 g), a required amount of SbF_5, and CF_3SO_3H (90 mmol, 13.40 g) were added into the flask, and the mixture was stirred vigorously at 0 °C. The

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amounts of SbF_5 in the solutions in the flask and the added solutions were controlled so both solutions would be considered to have the same SbF_5 concentrations, taking into account the consumption of SbF_5 to protonate *m*-xylene. After 1 min, the reaction was quenched in ice−water and the mixture extracted with benzene, and the product yields were determined using GC with an internal standard.

Formylation Procedures of Method B in $CF_3SO_3H-SbF_5$. A required amount of SbF_5 and CF_3SO_3H (200 mmol, 30.00 g) were put into a 300 mL three-necked flask equipped with a CO gas buret under atmospheric pressure at 0 °C. *m*-Xylene (10 mmol, 1.06 g) was added into the flask and the mixture stirred vigorously at 0 °C. After 1 min, the reaction was quenched in ice−water and the mixture extracted with benzene, and the product yields were determined using GC with an internal standard.

Reaction Procedures in FSO_3H-SbF_5. A required amount of SbF_5 and FSO_3H (174 mmol, 17.40 g) were put into a 300 mL three-necked flask equipped with a CO gas buret under atmospheric pressure. Alkylbenzene (20 mmol) was added over 30 min into FSO_3H-SbF_5 and the mixture stirred vigorously at 0 °C. After the addition was complete, the temperature was kept at 0 °C for 1 h, and the temperature was then increased to room temperature. The reaction was quenched in ice−water and the mixture extracted with benzene. The yields of the products were determined using GC with an internal standard, and the products were characterized using IR, ^{1}H-NMR, ^{13}C-NMR, mass spectra, and elemental analysis after isolation by vacuum distillation and recrystallization.

Synthetic Procedure of CH_3COF. HF (0.5 mol, 10.0 g) was placed into a 200 mL Teflon flask at 0 °C. $(CH_3CO)_2O$ (0.6 mol, 61.2 g) was slowly added dropwise into the flask and the mixture stirred at 0 °C. After 3 h, the CH_3COF was separated from the reaction mixture in 70% yield by distillation.

Physical Properties for New Compounds. 3-Formyl-2,4,6-trimethylbenzenesulfonyl Fluoride. IR (KBr): 1695 (C=O), 1400, 1200 (SO_2F) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.58 (s, 3H), 2.70 (s, 3H), 2.79 (d, 3H, J = 2.4 Hz), 7.22 (s, 1H), 10.74 (s, 1H). ^{13}C-NMR ($CDCl_3$): δ 17.2, 17.3, 20.6, 23.2, 131.7, 132.1, 134.3, 134.5, 141.9, 143.8, 145.9, 192.7. Anal. Found: C, 51.80; H, 4.76; M$^+$, 230. Calcd for $C_{10}H_{11}O_3SF$: C, 52.16; H, 4.81; M, 230.

5-Formyl-2,3,4-trimethylbenzenesulfonyl Fluoride. IR (KBr): 1690 (C=O), 1385, 1205 (SO_2F) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.39 (s, 3H), 2.70 (s, 6H), 8.37 (s, 1H), 10.39 (s, 1H). ^{13}C-NMR ($CDCl_3$): δ 15.9, 16.0, 17.9, 131.1, 131.6, 132.5, 141.1, 142.1, 146.6, 190.6. Anal. Found: C, 52.01; H, 4.76; M$^+$, 230. Calcd for $C_{10}H_{11}O_3SF$: C, 52.16; H, 4.81; M, 230.

2-Formyl-3,4,5,6-tetramethylbenzenesulfonyl Fluoride. IR (KBr): 1680 (C=O), 1375, 1180 (SO_2F) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.24 (s, 3H), 2.36 (s, 3H), 2.58 (s, 3H), 2.61 (s, 3H), 10.49 (s, 1H). ^{13}C-NMR ($CDCl_3$): δ 16.3, 17.2, 17.8, 19.3, 19.4, 132.5, 132.8, 136.2, 136.3, 137.6, 141.2, 142.5, 195.2. Anal. Found: C, 54.01; H, 5.39; M$^+$, 244. Calcd for $C_{11}H_{13}O_3SF$: C, 54.09; H, 5.36; M, 244.

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