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Unusual Rate Acceleration in Brønsted Acid Catalyzed Dehydration Reactions: Local Hydrophobic Environment in Aggregated *N*-(2,6-diphenylphenyl)-*N*-mesitylammonium Pentafluorobenzenesulfonates

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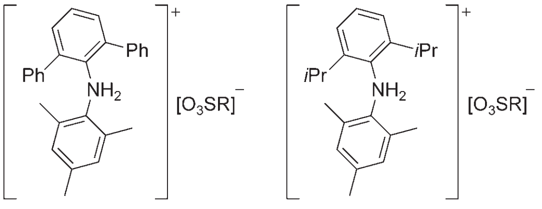
Abstract: Bulky diarylammonium pentafluorobenzenesulfonates effectively promote dehydration reactions, such as condensation reactions to give esters and the dehydrative cyclization of 1,3,5-triketones. In particular, *N*-(2,6-diphenylphenyl)-*N*-mesitylammonium pentafluorobenzenesulfonate shows much higher catalytic activity than $C_6F_5SO_3H$ under reaction conditions without the removal of generated water, even though the former is a weaker acid. Its crystallization gives an aggregated cyclic ion pair, which is composed of two diarylammonium cations, four pentafluorobenzenesulfonate anions, and two oxonium cations. This ion pair is strongly stabilized by four intermolecular and two intramolecular π–π attractive interactions and 10 hydrogen bonds. The extremely high catalytic activity of *N*-(2,6-diphenylphenyl)-*N*-mesitylammonium pentafluorobenzenesulfonate in the dehydration reactions may be ascribed to the local hydrophobic environment of the tightly aggregated ammonium salts.

Keywords: aggregation · ammonium salts · condensation · dehydration · homogeneous catalysis

Introduction

Acid-catalyzed dehydration reactions, such as condensation reactions to form esters, are among the most fundamental reactions. More environmentally benign alternatives are in strong demand by the chemical industry. Some ammonium salts have been developed as mild Brønsted acid dehydration catalysts. In 2000, Tanabe and co-workers reported that diphenylammonium triflate ($[Ph_2NH_2]^+[OTf]^-$) catalyzed efficiently the condensation of carboxylic acids with equimolar amounts of alcohols to give esters.[1] In 2005, we reported the bulky diarylammonium pentafluorobenzenesulfonates **1a** and **2a**, which are much milder Brønsted acids than the corresponding ammonium triflates, to be extremely active condensation catalysts for the formation of esters (Scheme 1).[2,3] Interestingly, the bulkier catalyst **1a**, which was formed from an equimolar mixture of *N*-(2,6-diphenylphenyl)-*N*-mesitylamine and pentafluorobenzenesulfonic acid ($C_6F_5SO_3H$), exhibited higher catalytic activity than $C_6F_5SO_3H$ in the dehydrative condensation of 4-phenylbutyric acid with an equimolar amount of cyclododecanol under reaction conditions without the removal of water, despite the weaker acidity of **1a** (Figure 1).[2b] In contrast, **2a** showed catalytic activity similar to that of $C_6F_5SO_3H$, whereas the catalytic activity of $[Ph_2NH_2]^+[OTf]^-$ was lower than that of $C_6F_5SO_3H$. It was hypothesized that the hydrophobic environment created around the ammonium hydrogen atoms in the diarylammonium pentafluorobenzenesulfonates promoted the dehydrative condensation reaction, and that the steric bulk of the catalyst suppressed the dehydrative elimination of secondary alcohols to produce alkenes.



1a: R = C_6F_5
1b: R = Tol

2a: R = C_6F_5
2b: R = Tol

Scheme 1. Bulky diarylammonium arene sulfonates. Tol = tolyl.

During the course of our studies, we found that bulky diarylammonium pentafluorobenzenesulfonates promoted the dehydrative cyclization of 1,3,5-triketones to γ-pyrones[4]

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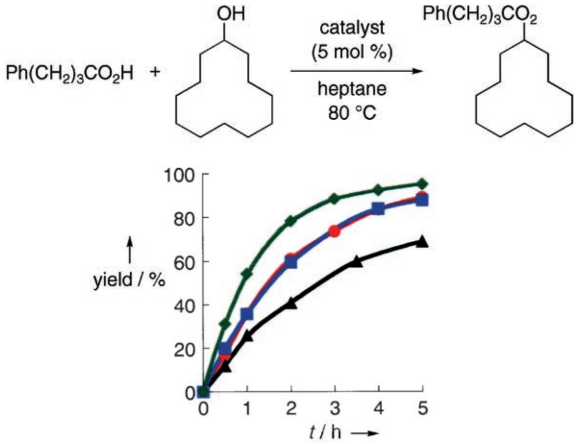


Figure 1. Condensation reaction of 4-phenylbutyric acid with an equimolar amount of cyclododecanol catalyzed by **1a** (green), **2a** (blue), $C_6F_5SO_3H$ (red), and $[Ph_2NH_2]^+[OTf]^-$ (black).[2b]

much more effectively than the condensation reaction for ester formation. 1,3,5-Triketones are generally less polar than carboxylic acids and alcohols. Therefore, if the local hydrophobic environment created around the ammonium hydrogen atoms in bulky diarylammonium pentafluorobenzenesulfonates is the key to the unusual acceleration of dehydration reactions, it should promote the dehydrative cyclization of 1,3,5-triketones much more efficiently than the condensation of carboxylic acids and alcohols. We investigated in detail the relationship between the catalytic activity of diarylammonium sulfonate catalysts and steric and stereoelectronic factors in the dehydrative cyclization of 1,3,5-triketones. Herein we also discuss the microscopic hydrophobic environment created in the aggregated diarylammonium sulfonates on the basis of their X-ray single-crystal structures.

Results and Discussion

We compared previously the catalytic activities of **2a** and $[Ph_2NH_2]^+[OTf]^-$ under reflux conditions without the removal of water and under azeotropic reflux conditions with the removal of water in the condensation reaction of 4-phenylbutyric acid with 6-undecanol in hexane.[2] Whereas the condensation reaction to form the corresponding ester was slightly decelerated under the catalysis of $[Ph_2NH_2]^+[OTf]^-$ when water was not removed, the reaction catalyzed by **2a** proceeded very well and was not influenced by water. To evaluate the catalytic activity of **2a** in the dehydrative cyclization of 4,6-dimethylnonane-3,5,7-trione (**3a**) in detail, the catalytic activities of **2a** and $C_6F_5SO_3H$ were compared upon heating without the removal of water and under azeotropic reflux conditions with the removal of water (Figure 2). Whereas the reaction catalyzed by $C_6F_5SO_3H$ at 80 °C without the removal of water gave γ-pyrone **4a** in 74 % yield after 8 h (red line, Figure 2a), the reaction under azeotropic reflux conditions in cyclohexane (b.p. 80.7 °C) with the removal of water gave **4a** in 96 % yield after the same reaction time (blue line, Figure 2a). The reaction catalyzed by $C_6F_5SO_3H$ was considerably decelerated when water was not removed. However, the reaction proceeded more rapidly in perfluoromethylcyclohexane, which is a water-repellent solvent, without the influence of water to give **4a** quantitatively after 8 h (green line, Figure 2a).[5] It seems that fluorous media release the water produced from the active site of the catalyst. In contrast, the reaction catalyzed by **2a** at 80 °C gave **4a** quantitatively regardless of the conditions used (Figure 2b). Importantly, **2a** exhibited much higher catalytic activity than $C_6F_5SO_3H$ under conditions of heating without the removal of water, despite the weaker acidity of **2a**. These experimental results showed that the use of **2a** had the same rate-accelerating effect on the dehydrative cyclization of **3a** as the use of Dean–Stark conditions and the use of more hydrophobic perfluoromethylcyclohexane as the solvent instead of heptane or cyclohexane.

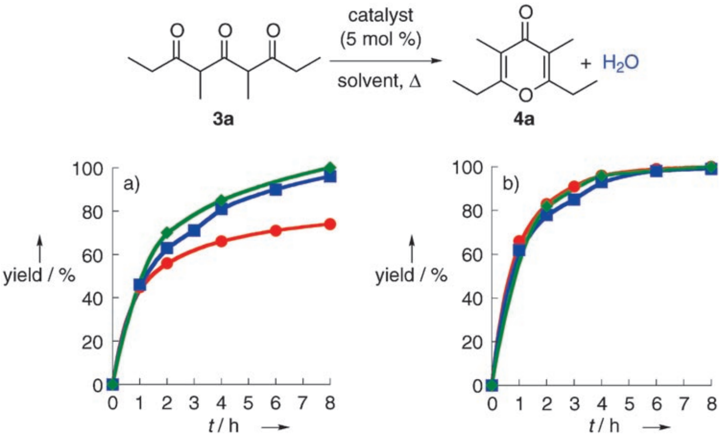


Figure 2. Dehydrative cyclization of 4,6-dimethylnonane-3,5,7-trione (**3a**; 0.2 mmol) in solvent (4 mL) catalyzed by a) $C_6F_5SO_3H$ and b) **2a**. The yield of γ-pyrone **4a** was evaluated by HPLC analysis. Red: heptane, 80 °C, without removal of water; blue: cyclohexane (b.p. 80.7 °C), azeotropic reflux, with removal of water; green: perfluoromethylcyclohexane, 80 °C.

Abstract in Japanese:

嵩高いジアリールアンモニウムペンタフルオロベンゼンスルホナートがエステル縮合のみならず1,3,5-トリケトンの脱水環化反応に対しても優れた触媒活性を示した。最も触媒活性の高い**1a**の再結晶操作によって得られる**5**は、X線結晶構造解析により、嵩高いアリール基がアンモニウムカチオンを覆う逆ミセルのような会合構造であり、アリール基の分子内および分子間π–π相互作用によって安定化されていることが明らかとなった。これらのアリール基によって形成された局所的な疎水環境が反応の進行に伴って生成する水を触媒活性部位から効果的に排除し、触媒は失活することなく脱水反応を促進すると考えられる。

We then investigated the solvent effect for the dehydrative cyclization of **3a** catalyzed by **2a** or $C_6F_5SO_3H$ without the removal of water (Table 1). When the reaction catalyzed by **2a** was conducted in heptane at 80 °C for 8 h, **4a** was ob-

Table 1. Dehydrative cyclization of **3a** to **4a** catalyzed by **2a** or $C_6F_5SO_3H$.[a]

$$\mathbf{3a} \xrightarrow[\text{heptane, 80 °C, 8h}]{\text{catalyst (5 mol \%)}} \mathbf{4a} + H_2O$$

Entry	Solvent	Yield of **4a** [%][b]	
		2a	$C_6F_5SO_3H$
1	heptane	100	74
2	toluene	56	55
3	1,4-dioxane	64	58
4	EtCN	64	61

[a] Reaction conditions: **3a** (0.2 mmol), catalyst (5 mol %), solvent (4 mL), 80 °C, 8 h; water generated was not removed. [b] Determined by HPLC analysis.

tained in quantitative yield (Table 1, entry 1). On the other hand, in the more polar solvents toluene, 1,4-dioxane, and propionitrile (EtCN), the reaction gave **4a** in 56–64 % yield (Table 1, entries 2–4). Similarly, the reaction catalyzed by $C_6F_5SO_3H$ proceeded better in heptane than in toluene, 1,4-dioxane, or EtCN (Table 1, entry 1 vs. entries 2–4). Interestingly, **2a** and $C_6F_5SO_3H$ had similar catalytic activities in toluene, 1,4-dioxane, and EtCN (Table 1, entries 2–4), whereas **2a** showed much higher catalytic activity than $C_6F_5SO_3H$ in heptane (Table 1, entry 1). In less polar solvents, such as heptane, **2a** should form a stable ion pair in which the ammonium cation is tightly surrounded by two bulky *N*-aryl groups and an *S*-pentafluorophenyl group. It is conceivable that the water generated in the reaction is released rapidly from the active site of **2a** as a result of the hydrophobic environment created by these bulky aryl groups, and that the hydrophobic wall prevents polar water from gaining access to the active site of **2a**. On the other hand, we hypothesize that **2a** cannot form a stable ion pair in polar solvents, such as toluene, 1,4-dioxane, and EtCN, and that for this reason no rate-accelerating effect was observed in these solvents.

In condensation reactions to give esters, the catalytic activities of diarylammonium tosylates were similar to that of *p*-toluenesulfonic acid (TsOH) and almost independent of the structures of the diarylamines, whereas the catalytic activities of diarylammonium pentafluorobenzenesulfonates depended on the structures of the diarylamines.[2b] The catalytic activity of $C_6F_5SO_3H$, TsOH, and their diarylammonium salts in the dehydrative cyclization of 4,6,9-trimethyldecane-3,5,7-trione (**3b**) to γ-pyrone **4b** was examined in heptane at 80 °C without the removal of water (Figure 3). Compound **3b**, which has a methyl group at the 9-position, is less reactive than **3a** because of the steric hindrance of the methyl group. As in the condensation reactions to form esters, the diarylammonium tosylates showed slightly lower catalytic activities than that of TsOH in the dehydrative cyclization of **3b** (Figure 3 a, specific acid catalysis).[6] In contrast, the catalytic activities of the diarylammonium pentafluorobenzenesulfonates depended strongly on the structures of the diarylamines (Figure 3 b, general acid catalysis).[6] TsOH ($pK_a = 8.5$ in CD_3CO_2D) is a stronger acid than $C_6F_5SO_3H$ ($pK_a = 11.1$ in CD_3CO_2D).[2,7,8] As a result of its weaker acidity and slight hydrophobicity, diphenylammonium pentafluorobenzenesulfonate ($[Ph_2NH_2]^+[O_3SC_6F_5]^-$, black line) showed lower catalytic activity than $C_6F_5SO_3H$ (red line), whereas **1a** (green line) and dimesitylammonium pentafluorobenzenesulfonate ($[Mes_2NH_2]^+[O_3SC_6F_5]^-$, blue line) exhibited significantly higher catalytic activities than that of $C_6F_5SO_3H$. In particular, the bulkiest catalyst, **1a**, had the highest catalytic activity because of its efficient creation of a local hydrophobic environment. Interestingly, **1a** exhibited higher catalytic activity than TsOH despite the much weaker acidity of **1a** (red line, Figure 3 a vs. green line, Figure 3 b). These experimental results suggested that the two bulky *N*-aryl groups and the *S*-pentafluorophenyl group, which surround the active site (NH_2^+) of **1a**, accelerate the dehydration reactions synergistically. On the basis of the results in Figure 2, Figure 3, and Table 1, the rate-accelerating effect on the **1a**-catalyzed dehydration reaction could be attributed to the local hydrophobic environment in **1a**. As expected, the dehydrative cyclization of 1,3,5-triketones was promoted much more effectively than the condensation reaction to form esters.[9]

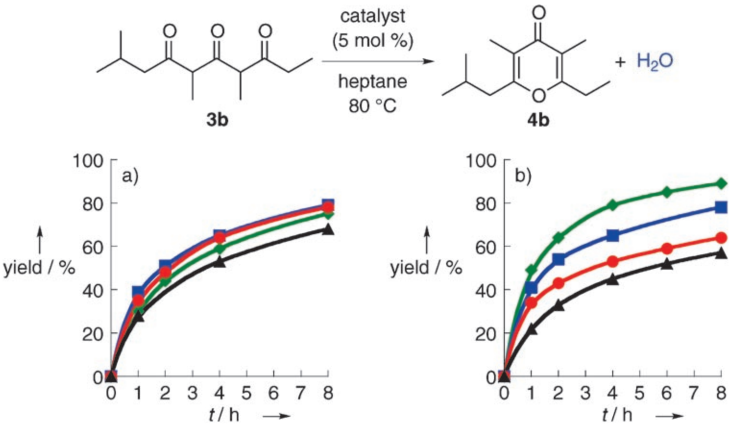
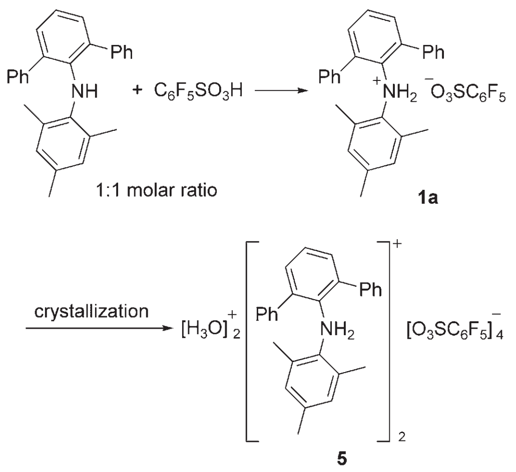


Figure 3. Dehydrative cyclization of 4,6,9-trimethyldecane-3,5,7-trione (**3b**) catalyzed by a) diarylammonium tosylates and b) diarylammonium pentafluorobenzenesulfonates. The yield of γ-pyrone **4b** was evaluated by HPLC analysis. Substituents on the ammonium cation: green: $[(2,6\text{-}Ph_2C_6H_3)MesNH_2]^+$; blue: $[Mes_2NH_2]^+$; red: H^+; black: $[Ph_2NH_2]^+$.

X-ray single-crystal structures of the diarylammonium sulfonates suggested that a hydrophobic environment in their aggregates might play a role in their observed reactivity.[10] A crystal was obtained by the recrystallization from $CHCl_3$/hexane of **1a**, a 1:1 molar mixture of (2,6-diphenylphenyl)mesitylamine and $C_6F_5SO_3H$ (Scheme 2). Surprisingly, X-ray crystallographic analysis revealed that the crystal consisted of a supramolecular complex **5** composed of two diarylammonium cations, four pentafluorobenzenesulfonate anions, and two oxonium cations (Figure 4).[11] Interestingly, in the crystal structure, two ammonium cations and two oxonium cations are surrounded by 12 hydrophobic aryl groups in a similar arrangement to that observed for reverse micelles. Furthermore, the cyclic ion pair is stabilized thermodynamically and conformationally not only by four $HN^+{-}H\cdots O{=}SO_2^-$ and six $H_2O^+{-}H\cdots O{=}SO_2^-$ intermolecular hydrogen bonds, but also by two intermolecular π–π interactions be-



Scheme 2. Formation of **5** by the crystallization of **1a**.

tween mesityl and pentafluorophenyl groups, two intermolecular π–π interactions between phenyl and pentafluorophenyl groups, and two intramolecular π–π interactions between mesityl and phenyl groups.[9] The distance between the mesityl and pentafluorophenyl groups is 3.6–3.8 Å, and that between the mesityl and phenyl groups is 3.0–3.6 Å. The extremely high catalytic activity of **1a** in the esterification and in the dehydrative cyclization of 1,3,5-triketones may be ascribed to the hydrophobic environment around the ammonium hydrogen atoms in **5**, which accepts carboxylic acid groups or 1,3,5-triketones in place of water.

The X-ray single-crystal structure of $[Mes_2NH_2]^+[O_3SC_6F_5]^-$ is a dimeric complex composed of two dimesitylammonium cations and two pentafluorobenzenesulfonate anions: $[Mes_2NH_2]^+{}_2[O_3SC_6F_5]^-{}_2$ (Figure 5). The ammonium cation moiety is surrounded by six aryl groups, and the cyclic ion pair is also stabilized by two intermolecular π–π interactions. The distance between the mesityl and pentafluorophenyl groups is 3.5–3.6 Å. Dimesitylammonium tosyl-

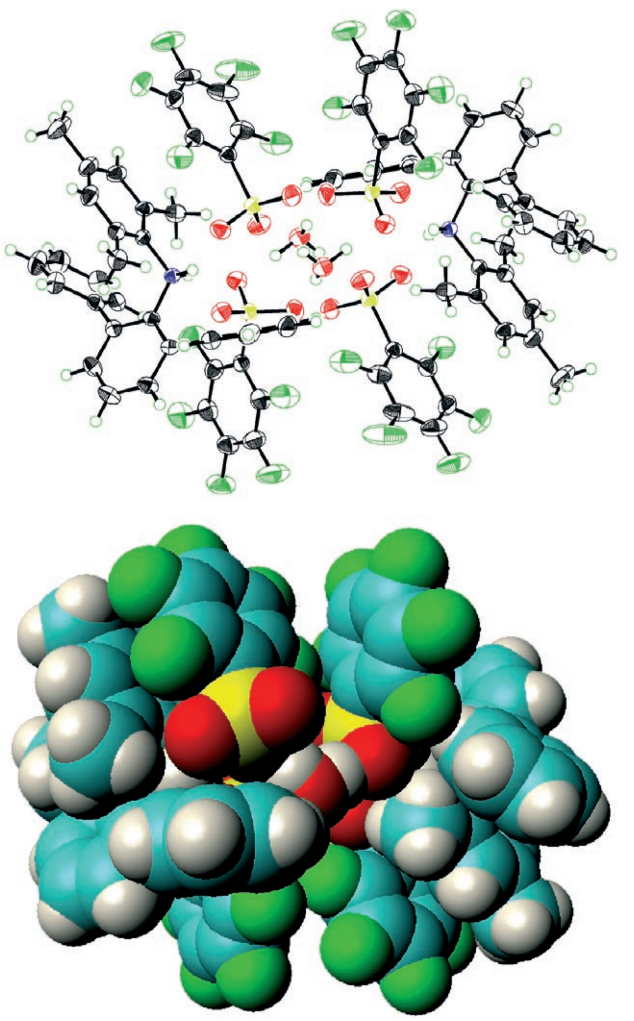


Figure 4. X-ray single-crystal structure of **5**. Top: ORTEP diagram (ellipsoids drawn at 50% probability); bottom: space-filling diagram. F = green, N = blue, O = red, S = yellow.

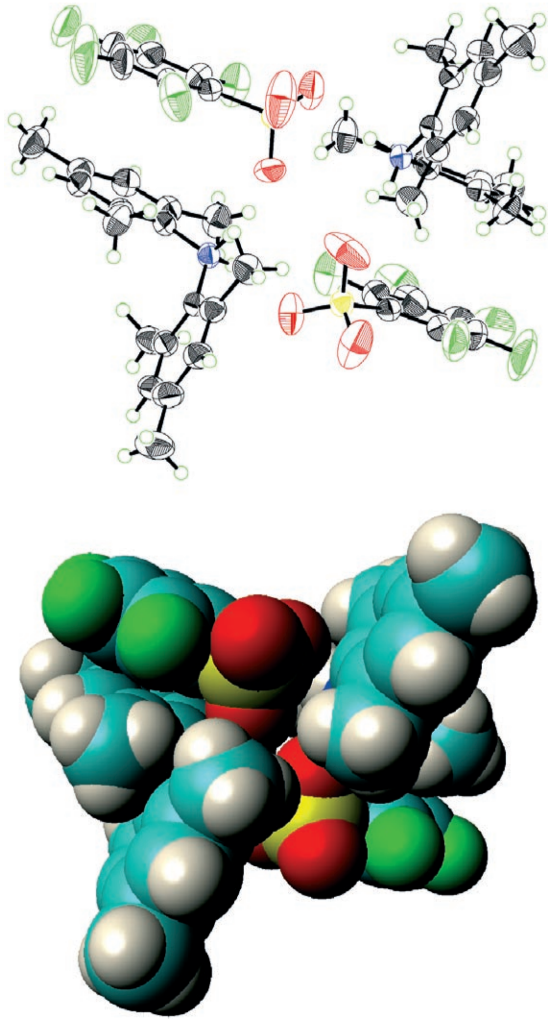


Figure 5. X-ray single-crystal structure of $[Mes_2NH_2]^+{}_2[O_3SC_6F_5]^-{}_2$. Top: ORTEP diagram (ellipsoids drawn at 50% probability); bottom: space-filling diagram. F = green, N = blue, O = red, S = yellow.

ate ($[Mes_2NH_2]^+[OTs]^-$) also formed a complex composed of two dimesitylammonium cations and two *p*-toluenesulfonate anions, $[Mes_2NH_2]^+{}_2[OTs]^-{}_2$ (Figure 6). In contrast to **5** and $[Mes_2NH_2]^+{}_2[O_3SC_6F_5]^-{}_2$, $[Mes_2NH_2]^+{}_2[OTs]^-{}_2$ does not exhibit intermolecular π–π interactions between the mesityl and tolyl groups. Unlike the diarylammonium sulfonates, anilinium pentafluorobenzenesulfonate did not form a cyclic-ion-pair structure (Figure 7). Therefore, we conclude that the presence of diarylamine units is important for the formation of cyclic ion pairs, the ammonium cation moieties in which are surrounded by aryl groups.

Catalyst **1a** and $[Mes_2NH_2]^+[O_3SC_6F_5]^-$, which had excellent rate-accelerating effects on the dehydration reactions examined, formed aggregated cyclic ion pairs **5** and $[Mes_2NH_2]^+{}_2[O_3SC_6F_5]^-{}_2$. These ion pairs might be the real active species. They are stabilized not only by intermolecular hydrogen bonds but also by intermolecular π–π interactions between the mesityl and pentafluorophenyl groups. Moreover, the use of the less polar solvent heptane also promoted tight aggregation between the diarylamines and $C_6F_5SO_3H$, which is less acidic and less polar than TsOH. In contrast, $[Mes_2NH_2]^+[OTs]^-$ was less active as a dehydration catalyst because of the instability of the cyclic ion pair owing to the absence of intermolecular π–π interactions and to the more acidic and more polar nature of TsOH. Therefore, it seems that the catalytic activity of $[Mes_2NH_2]^+$ $[OTs]^-$ derives mainly from its strong acidity. The formation of a stable cyclic ion pair in which the ammonium hydrogen atoms are located in the local hydrophobic environment is crucial for excellent catalytic activity.

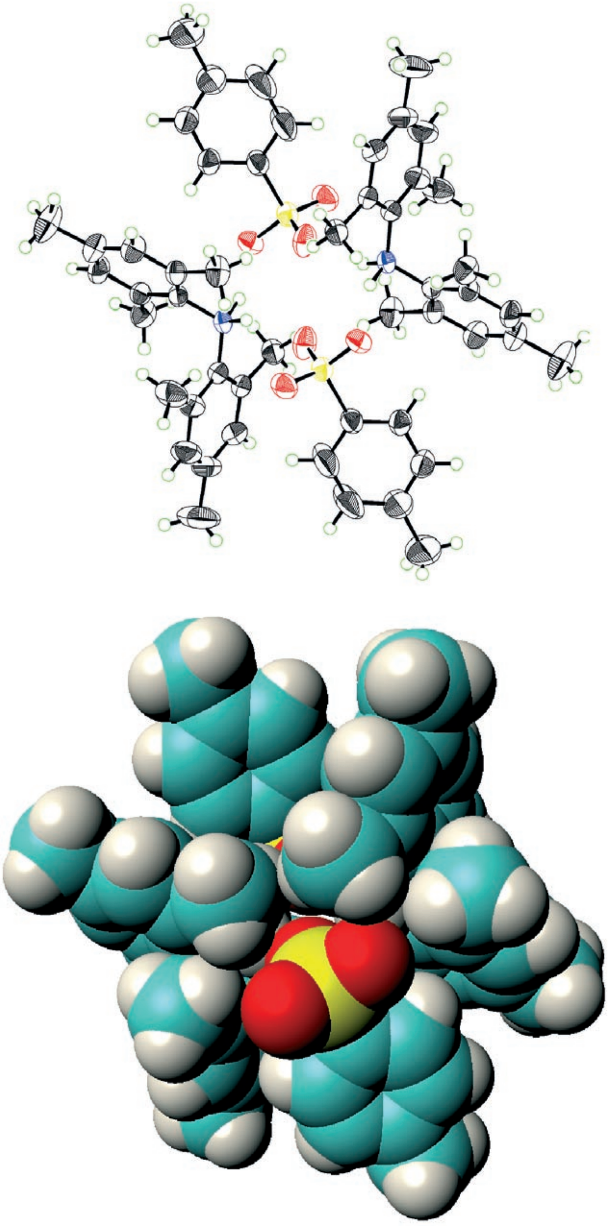


Figure 6. X-ray single-crystal structure of $[Mes_2NH_2]^+{}_2[OTs]^-{}_2$. Top: ORTEP diagram (ellipsoids drawn at 50 % probability); bottom: space-filling diagram. N = blue, O = red, S = yellow.

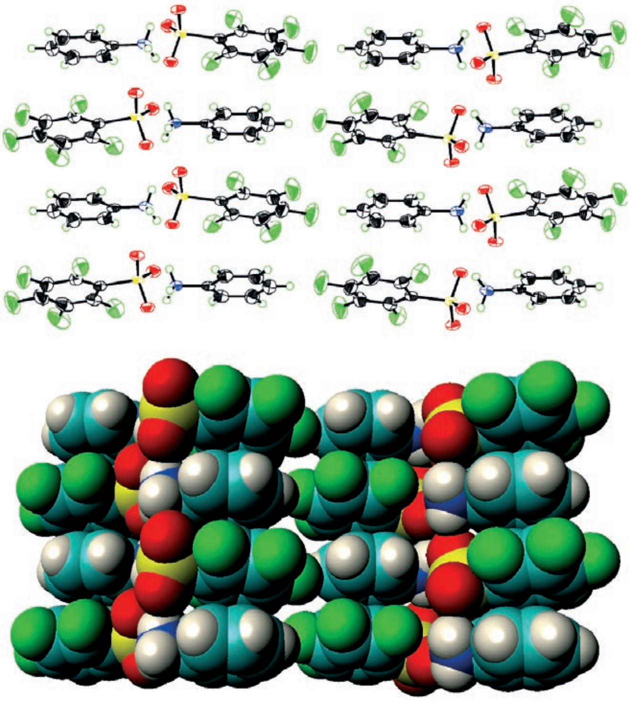
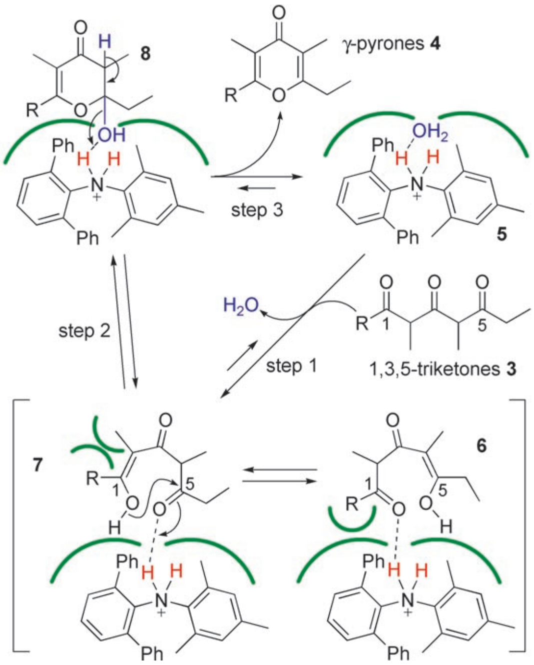


Figure 7. X-ray single-crystal structure of anilinium pentafluorobenzenesulfonate. Top: ORTEP diagram (ellipsoids drawn at 50 % probability); bottom: space-filling diagram. F = green, N = blue, O = red, S = yellow.

Water molecules produced at the active site of the bulky ammonium pentafluorobenzenesulfonates are exchanged readily for less polar substrates, such as carboxylic acids and 1,3,5-triketones. Once water molecules are released from the ammonium cation moiety, a hydrophobic wall prevents polar water molecules from gaining access to the active site of the catalysts and thus inhibits the inactivation of the catalyst by water. In contrast, less polar substrates can approach the active site through the hydrophobic wall and be activated efficiently. Thus, the bulky diarylammonium pentafluorobenzenesulfonates exhibited remarkable catalytic activities in the dehydration reactions, and their catalytic activity did not decrease even under reaction conditions without the removal of water. In contrast, the sulfonic acids interact with water more strongly than with less polar substrates. Therefore, sulfonic acids are inactivated when water is not removed from the reaction media.

A proposed mechanism for the dehydrative cyclization of 1,3,5-triketones is shown in Scheme 3. The bulky ammonium catalyst **5** (represented simplistically as the active catalytic unit) should coordinate preferentially with the carbonyl oxygen atom at the 5-position of 1,3,5-triketones **3** over that at the 1-position, to avoid the steric hindrance of the R group (step 1). However, the enol intermediate **7** is less stable than **6** because of steric effects between the R group and the methyl group. Therefore, **3b**, in which R is an isobutyl group, is less reactive than **3a**, which has an ethyl group at this position. Compound **7** is converted reversibly into the cyclic hemiacetal **8** (step 2). The coordination of **5** with the hydroxy group of **8** should make the hydrophilic hemiacetal moiety of **8** labile in the hydrophobic environment, and the dehydration of **8** (step 3) is promoted. Dehydration is also promoted by the steric bulk of **5**, and thus **8** is converted readily into the corresponding γ-pyrones **4**. The water generated is released rapidly from the active site of **5** and exchanged readily for less polar **3** because of the hydrophobic environment (step 1). Thus, compound **5** exhibits remarkable catalytic activity without being affected by the water generated.



Scheme 3. Proposed mechanism of the dehydrative cyclization of 1,3,5-triketones **3**. $C_6F_5SO_3^-$ is omitted for clarity.

Conclusions

Bulky diarylammonium pentafluorobenzenesulfonates show an unusual rate-accelerating effect in dehydration reactions, such as condensation reactions to form esters and the dehydrative cyclization of 1,3,5-triketones. In particular, the bulkiest hydrophobic catalyst, **1a**, showed much higher catalytic activity than $C_6F_5SO_3H$, even though **1a** is a weaker acid. It is conceivable that the local hydrophobic environment created by the tight aggregation of **1a** in low-polarity solvents is key to the efficient promotion of dehydration reactions. X-ray crystallographic analysis of **5**, which might be the real active species, suggested that the stabilization of the cyclic ion pair by intermolecular π–π interactions between hydrophobic bulky aryl groups was crucial for the creation of a hydrophobic environment.

Experimental Section

General

IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer. ^{1}H NMR spectra were recorded on a Varian Gemini-2000 spectrometer. Chemical shifts are given in ppm relative to tetramethysilane, which was included as an internal standard. ^{13}C NMR spectra were recorded on an INOVA spectrometer. Chemical shifts are given in ppm relative to the solvent resonance ($CDCl_3$, 77.0 ppm). Analytical HPLC was performed on a Shimadzu Model LC-6 A instrument with a Nomura Chemical Develosil 30–5 (4.6×250-mm) column. All experiments were carried out under an atmosphere of dry nitrogen. For preparative column chromatography, Merck silica gel 60 (0.040–0.063 mm) was used. High-resolution mass-spectral analysis (HRMS) was performed at the Chemical Instrument Room, Nagoya University. X-ray crystallographic analysis was performed with a Bruker SMART APEX diffractometer (graphite monochromator, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å), and the structures were solved by direct methods and expanded by using Fourier techniques (Sir97 and SHELXL[12]). Dry THF was purchased from Wako as "anhydrous" and stored under nitrogen. Diisopropylamine was freshly distilled from calcium hydride, and other materials were obtained from commercial suppliers and used without further purification. 4,6-Dimethylnonane-3,5,7-trione (**3a**) and γ-pyrone **4a** are known compounds.[13] The preparation of the ammonium-salt catalysts **1a**, **1b**, **2a**, and **2b** was reported previously.[2]

Syntheses and Spectral Data

General procedure: A mixture of a triketone **3** (0.2 mmol) and **1a** (6.1 mg, 0.01 mmol) in heptane (4 mL) was stirred at 80 °C for several hours. The reaction was then quenched with triethylamine (ca. 0.1 mL), and the reaction mixture was concentrated under reduced pressure. The yields of γ-pyrones **4** were determined by HPLC analysis on the basis of conversion of the starting material. The products were purified by column chromatography on silica gel by elution with a mixture of hexane and ethyl acetate.

3b: IR (neat): $\tilde{\nu} = 3402$, 1714, 1650, 1613, 1463, 1389, 1372, 1167, 1092, 1061, 1017 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.80$–1.40 (m, 14.8 H), 1.65–2.75 (m, 5.6 H), 3.60–3.90 (m, 1.2 H), 16.55 (s, 0.1 H), 16.66 ppm (s, 0.3 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 6.4$, 7.4, 7.5, 7.6, 7.8, 8.5, 8.6, 9.4, 9.6, 11.8, 12.3, 12.7, 12.9, 13.2, 22.3, 22.4, 22.5, 23.8, 24.0, 25.8, 26.8, 28.9, 30.2, 31.4, 33.8, 34.4, 34.5, 40.8, 40.9, 44.6, 45.3, 49.9, 50.1, 52.4, 52.6, 58.9, 59.1, 59.3, 59.7, 104.3, 104.4, 104.5, 104.8, 108.3, 108.9, 167.1, 167.4, 185.8, 190.3, 193.8, 194.9, 197.0, 198.5, 203.5, 204.3, 206.5, 206.8, 207.4, 207.6, 208.2 ppm; HRMS (FAB): *m/z* calcd for $C_{13}H_{23}O_3$: 227.1647 $[M+H]^+$; found: 227.1651.

4b: IR (neat): $\tilde{\nu}=1659$, 1601, 1460, 1421, 1374, 1174, 1309 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=0.96$ (d, $J=6.9$ Hz, 6H), 1.21 (t, $J=7.5$ Hz, 3H), 1.95 (s, 3H), 1.95 (s, 3H), 2.05 (m, 1H), 2.45 (d, $J=7.5$ Hz, 2H), 2.59 ppm (q, $J=7.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): $\delta=9.4$, 10.0, 11.4, 22.3, 24.7, 27.5, 40.1, 117.7, 119.1, 162.9, 164.3, 179.9 ppm; HRMS (FAB): m/z calcd for $C_{13}H_{21}O_2$: 209.1542 $[M+H]^+$; found: 209.1535.

Crystallography

Crystal data for **5** ($C_{39}H_{29}F_{10}NO_7S_2$): colorless, crystal dimensions $0.20\times0.20\times0.20$ mm^3, monoclinic, space group $P2_1/n$ (#14), $a=10.9397(9)$, $b=25.183(2)$, $c=14.4475(12)$ Å, $\beta=108.235(2)°$, $V=3780.4(6)$ Å^3, $Z=3$, $D_{\text{calcd}}=1.157$ g cm^{-3}, $F(000)=1344$, $\mu=0.182$ mm^{-1}, $T=293(2)$ K, 28258 reflections collected, 10064 independent reflections with $I>2\sigma(I)$ ($2\theta_{\max}=29.19°$); 648 parameters were used for the solution of the structure; non-hydrogen atoms were refined anisotropically; $R_1=0.0523$, $wR2=0.1090$, GOF = 0.976.

Crystal data for $[Mes_2NH_2]^+[O_3SC_6F_5]^-$ ($C_{24}H_{24}F_5NO_3S$): colorless, crystal dimensions $0.30\times0.30\times0.30$ mm^3, tetragonal, space group $I\bar{4}$ (#82), $a=16.7876(10)$, $b=16.7876(10)$, $c=16.691(2)$ Å, $\beta=90.00°$, $V=4704.0(7)$ Å^3, $Z=8$, $D_{\text{calcd}}=1.416$ g cm^{-3}, $F(000)=2080$, $\mu=0.204$ mm^{-1}, $T=223(2)$ K, 17894 reflections collected, 6243 independent reflections with $I>2\sigma(I)$ ($2\theta_{\max}=29.15°$); 403 parameters were used for the solution of the structure; non-hydrogen atoms were refined anisotropically; $R_1=0.0524$, $wR2=0.1253$, GOF = 1.030.

Crystal data for $[Mes_2NH_2]^+[OTs]^-$ ($C_{25}H_{31}NO_3S$): colorless, crystal dimensions $0.20\times0.20\times0.20$ mm^3, monoclinic, space group $P2_1/c$ (#14), $a=11.7761(12)$, $b=11.6353(12)$, $c=17.3287(17)$ Å, $\beta=91.014(2)°$, $V=2374.0(4)$ Å^3, $Z=4$, $D_{\text{calcd}}=1.191$ g cm^{-3}, $F(000)=912$, $\mu=0.161$ mm^{-1}, $T=223(2)$ K, 17573 reflections collected, 6316 independent reflections with $I>2\sigma(I)$ ($2\theta_{\max}=29.21°$); 286 parameters were used for the solution of the structure; non-hydrogen atoms were refined anisotropically; $R_1=0.0616$, $wR2=0.1529$, GOF = 1.027.

Crystal data for anilinium pentafluorobenzenesulfonate ($C_{12}H_8F_5NO_3S$): colorless, crystal dimensions $0.20\times0.20\times0.20$ mm^3, monoclinic, space group $P2_1/n$ (#14), $a=6.559(3)$, $b=28.044(12)$, $c=7.486(3)$ Å, $\beta=98.425(8)°$, $V=1362.1(10)$ Å^3, $Z=4$, $D_{\text{calcd}}=1.664$ g cm^{-3}, $F(000)=688$, $\mu=0.308$ mm^{-1}, $T=223(2)$ K, 8960 reflections collected, 3512 independent reflections with $I>2\sigma(I)$ ($2\theta_{\max}=29.22°$); 231 parameters were used for the solution of the structure; non-hydrogen atoms were refined anisotropically; $R_1=0.0825$, $wR2=0.1842$, GOF = 1.107.

CCDC-297282 (**5**), -297281 ($[Mes_2NH_2]^+[O_3SC_6F_5]^-$), -604748 ($[Mes_2NH_2]^+[OTs]^-$), and -297280 (anilinium pentafluorobenzenesulfonate) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) or at www.ccdc.cam.ac.uk/conts/retrieving.html.

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[11] When the crystalline material **5** was used as a catalyst instead of a 1:1 molar mixture of $C_6F_5SO_3H$ and 2,6-(diphenylphenyl)mesitylamine, the esterification reaction of 4-phenylbutyric acid with cyclododecanol proceeded more slowly. An equilibrium mixture of **5** and 2,6-(diphenylphenyl)mesitylamine probably exists in a 1:1 molar solution of $C_6F_5SO_3H$ and 2,6-(diphenylphenyl)mesitylamine in heptane. These experimental results suggest that the ratio of **5** to 2,6-(diphenylphenyl)mesitylamine in a 1:1 molar solution of $C_6F_5SO_3H$ and 2,6-(diphenylphenyl)mesitylamine should be much higher than in a 2:1 molar solution of $C_6F_5SO_3H$ and 2,6-(diphenylphenyl)mesitylamine.

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