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Superacid and H-zeolite mediated reactions of benzaldehyde with aromatic compounds and cyclohexane. The role of mono- and dicationic intermediates

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Reactions of benzaldehyde (**1**) and related compounds–3-pyridinecarboxaldehyde (**9**) and acetophenone with benzene, chlorobenzene, *o*-dichlorobenzene and cyclohexane in the presence of superacids or H-form zeolite, HUSY were (re)investigated. In accordance with previous data, **1** condenses with benzene in triflic acid (CF_3SO_3H) as well as on HUSY to give triphenylmethane. At elevated temperature **1** also reacts with chlorobenzene but is inert towards *o*-dichlorobenzene. While **1** does not react with cyclohexane in $CF_3SO_3H{-}SbF_5$, **9** undergoes readily selective ionic hydrogenation to give 3-pyridilcarbinol (**14**). In the presence of excess of $AlCl_3$, however, as well as on HUSY, **1** reacts with cyclohexane to produce toluene. The mechanistic aspects of these reactions are discussed. Opposed to earlier, repeatedly cited suggestions that the reactivity of **1** involves, as in case of **9**, superelectrophilic diprotonated species, we show that a monocationic intermediate is the best rationale for these results.

KEY WORDS: superacids; zeolites; benzaldehyde; ionic hydrogenation; (super) electrophilic activation.

1. Introduction

Strong-acid induced condensation of benzaldehyde (**1**) with benzene is known since 1886 [1]. This classical reaction readily occurs in the presence of excess $AlCl_3$ [2] and belongs to a variety of hydroxyalkylation of aromatics [3]. The initially produced diphenylmethanol (**2**) quickly reacts with another molecule of benzene to give triphenylmethane (**3**) followed by appearance of a number of secondary products:diphenylmethane (**4**), triphenylmethanol and other compounds (scheme 1). More recently the same reaction was carried out in a liquid superacid, CF_3SO_3H (triflic acid, $Ho = -14.1$) and attracted considerable attention due to proposed key intermediacy of superelectrophilic [4] dications [5, 6]. As the monoprotonated benzaldehyde (**5**) can be already obtained with acidity of $Ho = -10$, the steady and linear increase in the reaction rate with further increase of acidity to $Ho = -18$ (triflic acid – CF_3CO_2H, SbF_5, $B(OSO_2CF_3)_3$ mixtures) has been rationalised by the increasing concentration of a diprotonated species **6,7** [5] or **8** [6]. Theoretical calculations show that dications **6** as well as **7** are 20.6 kcal/mol more stable than dications **8** [5]. Nevertheless, the absence of H/D exchange between the aromatic protons of benzaldehyde and CF_3SO_3D induced the authors to discard the intermediacy of **6** and **7** and suggest dications **8** as the only probable intermediate [6].

To us, however, the latter suggestion seemed improbable for the following reasons:

(1) The conversion of benzaldehyde into triphenylmethane (**1** → **3**) also takes place in the presence of HUSY zeolite [7], a solid acid the acidity of which has been estimated at $Ho \sim -6$ [8]. Generation of **8** can hardly occur on HUSY due to the comparatively low acidity and mainly because of discrete distribution of acidic sites on the solid.
(2) Even in the strongest superacids such as $HSO_3F{-}SbF_5$ no dications **8** (as well as **6** and **7**) could be observed [5] and, moreover, 4-methoxybenzaldehyde was diprotonated only on the carbonyl and the methoxy group [9]. In theory, O,O-diprotonation of a carbonyl group requires overcoming significant charge–charge repulsion and has still not been directly observed [10].
(3) A strong electrophile, such as dications **8** is expected to react readily with *o*-dichlorobenzene or at least chlorobenzene [11], but no reaction of **1** with these deactivated arenes was initiated by triflic acid [12].
(4) Acetophenone, which should be easier diprotonated under the same conditions as **1**, in fact does not react at all with benzene (in our experiments acetophenone did not react with benzene and toluene in 100 molar excess of triflic acid even at 130 °C for several hours).

The data we report in this paper on the reactivity of **1** towards different weak nucleophiles in various acidic

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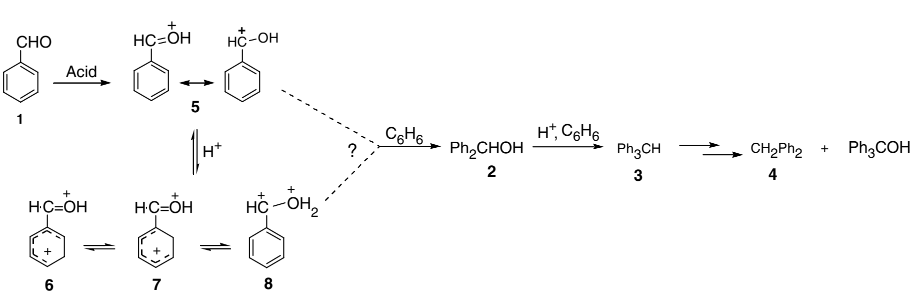


Scheme 1.

media provide a plausible explanation suggesting the monoprotonation seems the best rationale for all results presently available.

2. Experimental

2.1. Materials

Zeolite USY (Si/Al = 2.5, CBV500, Zeolyst International) in NH_4^+ form was activated at 550 °C overnight under air. Triflic acid, aluminum chloride and all organic reagents were purchased from suppliers (Acros and Aldrich) and used as received. Antimony pentafluoride was distilled twice under argon.

2.2. Experimental procedures

Typically, HUSY mediated reactions were carried out in 15 ml pressure tube loaded with activated zeolite (1 g, 4.67 mmol protonic sites), then with benzene (chlorobenzene, *o*-dichlorobenzene, C_6D_6 or cyclohexane, 3–5 ml) and **1** (20–1000 mg, 0.2–9 mmol). The resulting suspension was magnetically stirred at controlled temperature and allowed to react at a given period of time. After cooling, water (3 ml) was introduced to the reaction mixture followed by continuous solid–liquid extractions using ether as solvent. The combined organic phase was dried (Na_2SO_4) and analysed by GC (HP 5890) and GC–MS (CP 3800-Varian 1200). Then, in the case of the reactions of **1** with benzene (or C_6D_6) the resulting solutions were partially concentrated under reduced pressure and analysed by NMR (Bruker ADVANCE 300) to give the yields stated in scheme 4 and table 1.

2.3. Reaction of **1** with cyclohexane in the presence $AlCl_3$

Mixture of **1** (2 g, 19 mmol), cyclohexane (20 ml) and $AlCl_3$ (10 g, 75 mmol) was stirred at reflux temperature (~80°C) for 2 h and after cooling poured onto ice and extracted with CH_2Cl_2. The organic phase was washed with aqueous $NaHCO_3$, dried (Na_2SO_4) and analysed by and GC–MS and NMR.

2.4. Reactions of 3-pyridinecarboxaldehyde **9** with cyclohexane

(a) To a stirred solution of **9** (0.21 g, 2 mmol) in CF_3SO_3H (1.8 g, 12 mmol) at room temperature was added SbF_5 (1 g, 4.6 mmol). After the addition of cyclohexane (1 ml) the reaction mixture was stirred for 15 min and poured over several grams of ice. The resulting mixture was made basic with concentrated NaOH and extracted with $CHCl_3$. After evaporation of solvents, the crude product was purified by silica gel chromatography with CH_2Cl_2 to obtain 3-pyridilcarbinol **14** (0.17 g, 80%).

(b) A mixture of **9** (0.21 g, 2 mmol), $AlCl_3$ (1.34 g, 10 mmol) and cyclohexane (5 ml) was stirred at 90 °C for 15 h in pressure tube. The workup and chromatographic separation as described above offered compound **14** (0.065 g, 31%) and 3-methylpyridine **15** (0.033 g, 18%). NMR data of **14** [13] and **15** [14] were comparable with those previously reported.

3. Results and discussion

3.1. Acid mediated reactivity of benzaldehyde towards benzene, chlorobenzene and o-dichlorobenzene

Reaction of **1** with benzene in the presence of triflic acid is well documented [5,6,12,15]. It occurs under mild conditions, at room temperature [5] or at 50 °C [6] to give **3** in 30–90% yield along with secondary products. In the presence of HUSY (Si/Al 17.5) [16], providing ~1 molar equivalent of acidic (protonic) sites [17], **1** reacts slowly with benzene at 78 °C, but more readily at 150 °C to give **3** in 47% yield after 8 h along with traces of **4** [7].

The use of HUSY (Si/Al 2.5), providing a 25 molar excess of acidic sites appeared to be more efficient yielding 64% of **3** after 1 h at 130 °C (table 1). On the other hand, decreasing the ratio of the acid sites/**1** obviously decreases the efficiency of the catalysis, probably due to the influence of increasing adsorption of **1** [18]:the use of 4 molar excess of the acidic sites significantly slows down the reaction to give **3** (75%) along with **4** (10%) only after 60 h. However, even the use of catalytic amount of

Table 1
Results of the condensation of benzaldehyde (**1**) with benzene in the presence of HUSY (Si/Al 2.5) at 130 °C

Entry	Weight ratio of HUSY/**1**	An approximate molar ratio of the acidic sites/**1**	Reaction time (h)	Conversion (%)	Product (yield, %)[a]
1	50	25	1	96	**3** (64), **4** (15)
2	7.5	4	60	97	**3** (75), **4** (10)
3			14	9	**3** (1), **4** (4)
4	1	0.5	40	16	**3** (2), **4** (7)
5			60	22	**3** (2), **4** (10)

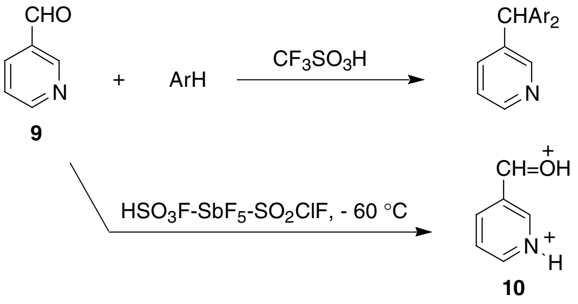
HUSY (the ratio of acidic sites/**1** = 0.5) does not completely suppress the reaction and offers a slow accumulation of **3** along with diphenylmethane in 5%, 9%, and 12% overall yields after 14, 40 and 60 h, respectively (table 1). Taking into account, that already known dicationic activation by HUSY of a variety of organic compounds is not catalytic at all but generally requires significant excess (~ 10) of the acidic sites [19], participation of dicationic species in reaction **1** → **3** on HUSY seems improbable.

Interaction of **1** with the less nucleophilic chlorobenzene in triflic acid necessitates temperatures well above 100 °C. It can also be performed in the presence of HUSY (Si/Al 2.5) at 150 °C. However, the reaction is slow (one half of conversion of **1** requires ~ 20 h, providing 100 molar excess of triflic acid or 5 molar excess of acidic sites, respectively) and yields a complex mixture of tri- and di-arylmethanes (scheme 2). Moreover, at 150 °C benzaldehyde does not react with *o*-dichlorobenzene even in the presence of excess triflic acid, $AlCl_3$ or HUSY as would be expected when superelectrophilic intermediates are suggested. Indeed, isoelectronic analogue of **1**, 3-pyridinecarboxaldehyde (**9**), readily reacts with benzene, chlorobenzene and *o*-dichlorobenzene at room temperature and even with nitrobenzene at elevated temperature in superacidic media [12]. Worth to note that the remarkable reactivity of **9** is convincingly explained by intermediacy of superelectrophilic N,O-diprotonated dications **10** and strongly supported by its NMR observation at low temperature (scheme 3) [12].

$$\mathbf{1} + \mathrm{PhCl} \xrightarrow[\text{or HUSY, 150 °C}]{CF_3SO_3H,\ 120\ °C} \mathrm{CHAr_3} + \mathrm{CH_2Ar_2}$$

Ar = Ph; o-, p-C_6H_4Cl

Scheme 2.



ArH = PhH, PhCl, o-$C_6H_4Cl_2$, $PhNO_2$

Scheme 3.

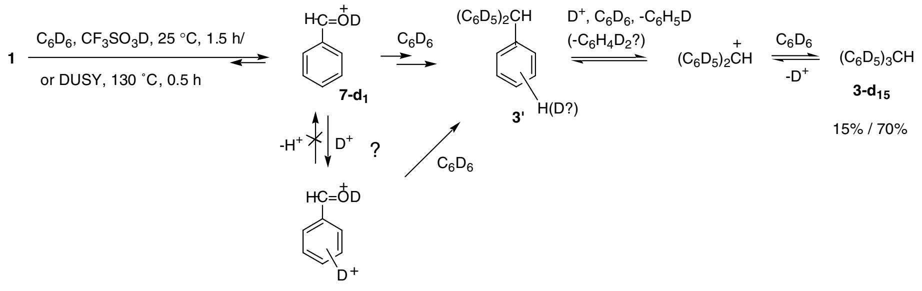
3.2. Proton deuterium exchange

The absence of H/D exchange on the aromatic ring of benzaldehyde was observed independently of the acid used D-USY or CF_3SO_3D, which allows to discard the intermediacy of dications **6** or **7**. When benzene-d_6 was used as reactant the final product was tri(pentadeuterophenyl)methane (**3**-d_{15}) and also no proton/deuterium exchange was observable in the recovered starting material (scheme 4). Unfortunately, these experiments cannot help to recognise the structure of an intermediate triarylmethane **3′**, which undergoes quick exchange with C_6D_6 to give exclusively **3**-d_{15}.

3.3. Reaction mechanism

Based on these considerations, we think that reactivity of **1** towards aromatic compounds in liquid acids as well as upon HUSY mediation has a common nature and involves monocations **5** as key reactive intermediate. This is in agreement with a decrease of reactivity in terms of acid catalyzed monocationic activation of following carbonyl compounds:Cl_3CCHO [3] > CH_2O [3], AlkCHO [3], $PhCOCF_3$[20], isomeric NO_2–C_6H_4-CHO [3,21], 4-$CF_3C_6H_4CHO$ [21] > **1** > $PhCOCH_3$ where **1** is the limiting compound still reacting with benzene. As was mentioned above, acetophenone, due to additional stabilisation of its O-protonated form by methyl group, does not react neither with benzene nor with toluene in triflic acid, but reacts however with toluene on HY-zeolite [22].

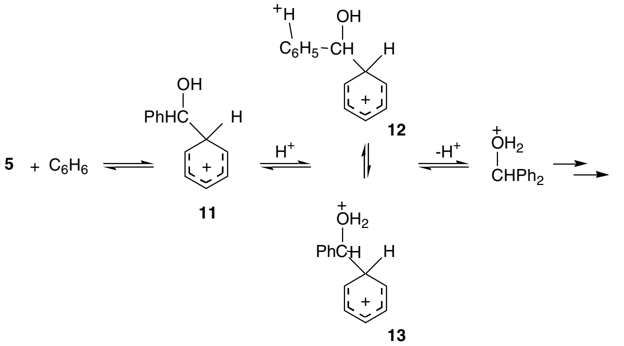
Increasing protosolvation of cations **11** with increasing acidity to shift the equilibrium to the right is most probably the best rationale for the effect of acidity on the rate of reaction (scheme 5). Therefore, preliminary formation of a dications and even more so O,O-diprotonated ions such as **8** are not needed to explain this effect. It is also relevant here to stress the role of acidity



Scheme 4.

as stressed by Olah for similar enhancement of reactivity of monocationic species in superacids [23] leading to the formation of the limiting dications (**12** or**13**) only in interaction with nucleophile (benzene).

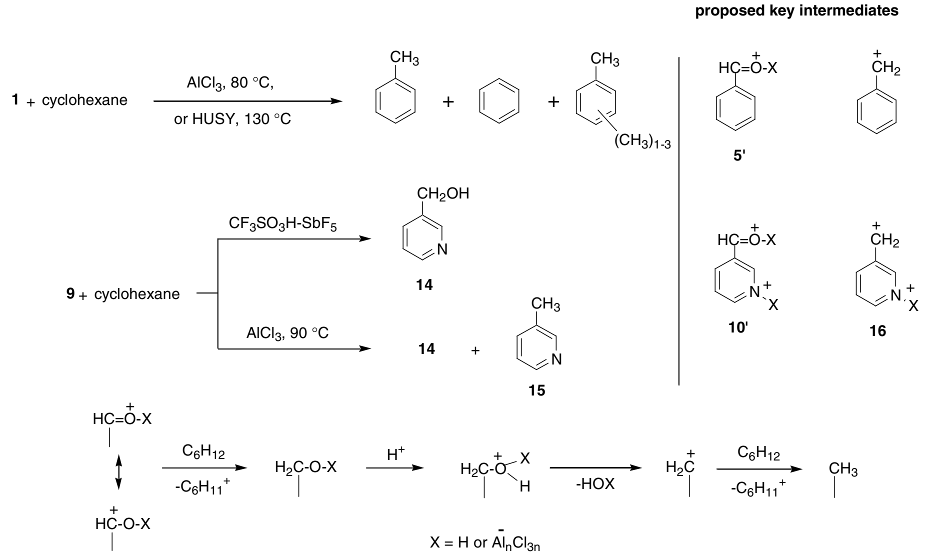
When reaction of **1** with benzene is mediated by HUSY, the energetically favourable solvation [18] of sufficiently polar alcohol **2** will help to shift the equilibrium to the right. The enhanced reactivity of acetophenone towards toluene on zeolite HY can be rationalised in the same way.



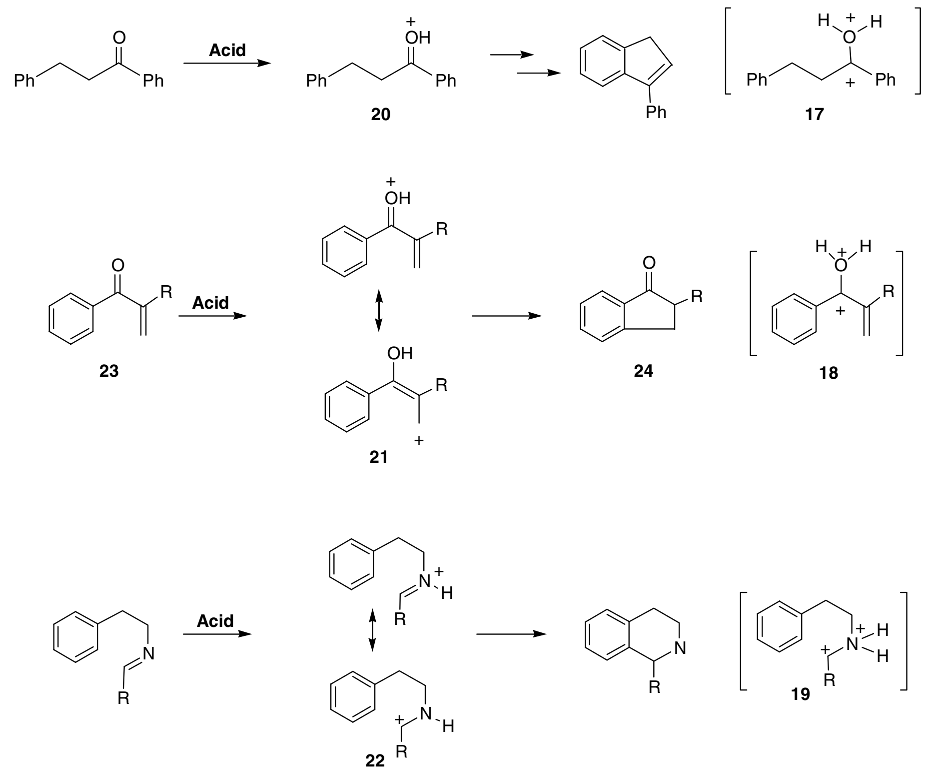
Scheme 5.

3.4. Acid catalyzed reduction of benzaldehyde with cyclohexane

Ionic hydrogenation of unsaturated carbonyl compounds by hydride transfer from alkanes in superacids has been successfully carried out by various authors [9a,10a,d,e,24]. However, with the exception of some heterocyclic ketones [24c,d] the carbonyl function generally stays intact. We found that benzaldehyde does not react with cyclohexane in superacidic conditions such as in triflic acid or CF_3SO_3H-SbF_5 system at 25–50 °C. On the other hand, it reacts with cyclohexane in the presence of 4 molar excess of $AlCl_3$ at 80 °C to give after 2 h toluene (~25%) along with its transalkylated [25] products:benzene (~35%), isomeric xylenes and tri- and tetra-methylbenzenes (~30%). Similarly **1** reacts with cyclohexane on HUSY (Si/Al 2.5, 7 molar excess of acidic sites) at 130 °C to give toluene as only initial product after 1 h (yield 7%), but a mixture of toluene (~ 50%), benzene (~20%) and xylenes (~20%) after 20 h (scheme 6). The notable difference between the $AlCl_3$and HUSY mediated reactions is only the production of stoichiometric amount of isomeric alkanes, $C_{12}H_{22}$ (in result of cyclohexane alkylation by the released $C_6H_{11}^+$ [24b]) in former reaction. The absence of



Scheme 6.



Scheme 7.

these alkanes in reaction mixtures in case of the HUSY mediated reaction can probably be explained by quick deprotonation of $C_6H_{11}^+$ to give cyclohexene followed by its disproportionation into benzene and cyclohexane [25a].

For comparison, acetophenone does not react with cyclohexane under any of these or more drastic conditions, using triflic acid (130 °C), $CF_3SO_3H{-}SbF_5$ (80 °C), $AlCl_3$ (130 °C) and HUSY (140 °C). In contrast, compound **9** reacts with cyclohexane:slowly in triflic acid, but readily, for 15 min at room temperature in $CF_3SO_3H{-}SbF_5$ to give 3-pyridilcarbinol (**14**) in 80% yield. Similar reaction also occurs in the presence of 5 molar excess of $AlCl_3$ at 90 °C to give mixture of **14** (~30%) and 3-methylpyridine (**15**, ~ 20%) along with starting material and byproducts. The formation of **14** and **15** can be related to selective ionic hydrogenation of corresponding dications **10′** and subsequently **16** with cyclohexane (scheme 6). That is similar to the mentioned reduction of heterocyclic ketones with cyclohexane in superacids, also proceeding through N,O-diprotonated intermediates [24c,d]. The difference in reactivity of **1** and **9** is considered to be in agreement with mono- and di-cationic character of key intermediates, according to scheme 6. Hydrogenation of $CH{=}O$ into CH_2OH is more efficient for **9** (providing strong protonic acidity) due to the increased electrophilicity of dications **10′**. However, the following reaction, **14** → **15** is not as efficient owing to unfavourable balance in stability-reactivity of the destabilised dications **16**.

3.5. Analogous reactivity of carbonyl compounds

We think that our explanation of the reactivity of **1**, involving the key intermediacy of monocationic, comparatively weak electrophiles instead of dicationic species might be widespread to similar reactions, such as electrophilic cyclizations presented in scheme 7. Despite that these reactions can be initiated by acids of moderate strength (Ho = −2.7 to −9), they have been suggested to proceed through O,O-(or N,N-)diprotonated dications **17**–**19** rather than monocations **20**–**22** also owing to the linear dependence of the reaction rates on acidity [26]. However, this dependence might be rationalised as it was done for **1** in scheme 5. In agreement with this suggestion, we found for example, that cyclization of **23** (R = CH_3) into corresponding indanone**24** readily occurs in the presence of catalytic amounts of HUSY, obviously supporting the key intermediacy of monocations **21** at least for the solid acid mediated reaction (in preparartion Please update if possible.). Worth to note, that a majority of reactions, which have been recognised to involve the key dicationic intermediates superelectrophiles) typically require as strong acid as triflic acid and often stronger superacids to be initiated [4,10,24].

4. Conclusion

(Super)acid as well as HUSY induced reactivity of **1** towards aromatics and cyclohexane is interpreted in terms of monocationic activation. The strong dependence of the reaction of **1** with benzene on acidity (or nature of acid) is rationalised by influence of the acid on the reactivity of intermediate **11**, rather than the necessity of additional protonation of monocations **5**. In general, similar dependence of the reactivity of comparatively weak, but still reactive electrophiles on acidity should be distinguished from the cases of direct superelectrophilic dicationic activation as for compound **9**.

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