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Communication

Coordination of Fluoro Ligands toward Sodium Ions Makes the Difference: Aqua Sodium Ions Act as Brønsted Acids in Polymerization of Vinyl Ethers and Styrenes

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In searching for aqua sodium species acting as Brønsted acids in catalysis, we explored the phenomenon that sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate dihydrate ($NaBAr^F_4$·$2H_2O$) evidently provides one proton source to initiate the polymerization of vinyl ethers in anhydrous dichloromethane solutions. In addition, $NaBAr^F_4$ catalyzed efficiently in the polymerization of activated styrenes, such as *p*-methoxystyrene.

The weakly coordinating and lipophilic nature of the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion ($BAr^F_4{}^-$), which was first utilized by Kobayashi et al. in 1981,[1] is of interest for a wide range of applications.[1−5] Metal ions associated with this fluorinated anion often show physical and chemical properties very different from those with common anions such as halides or even tetrafluoroborate.[2,3] In this context, quite a few highly reactive transition-metal species and their applications on catalysis have been investigated.[4−7] However, to the best of our knowledge, the chemical properties of the alkali-metal ions/tetrakis[3,5-bis(trifluoromethyl)phenyl]borate salts, particularly those of sodium salts, have been studied far less.[1a,4]

The sodium ion, being the sixth most abundant metallic ion in the earth's crust, is an important species in nature and is involved in a great number of chemical processes.[7] Like most metal ions, sodium ions are recognized as performing the role of a Lewis acid in chemical reactions. Thus, water molecules coordinate toward the metal ions, resulting in hydrated species, namely, $Na(H_2O)_n{}^+$, in which *n* is pending determination. Owing to its large polarizability, $Na(H_2O)_n{}^+$ can act as a proton donor with $pK_a \sim 14.2$, considered a weak acid.[8] Such an acidity makes the aqueous sodium chloride a neutral solution. Therefore, most acid-sensitive compounds are quite stable in a brine solution. To our knowledge, there is no precedent showing that aqua sodium species act as Brønsted acids to initiate a chemical reaction. We herein demonstrate for the first time that the hydrated sodium ion species can render a proton to initiate the polymerization of vinyl ether and methoxystyrene under anhydrous conditions. Moreover, this sodium salt also assists the hydrolysis of actals in an aqueous medium.

According to the reported procedure,[4,5b] we prepared sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate dihydrate via the reaction of [3,5-bis(trifluoromethyl)phenyl]magnesium bromide with sodium tetrafluoroborate in tetrahydrofuran, followed by the addition of water. Crystals suitable for the X-ray determination were obtained by recrystallizing the salt from a solution of ether/*n*-hexane with a trace of moisture. As shown in the ORTEP plot (Figure 1),[9] the sodium center displays a slightly distorted octahedral geometry with coordination of four fluorine atoms from trifluoromethyl groups and two water molecules arranged in a trans orientation. Upon close examination, the coordinating trifluoromethyl groups around the sodium ion originate

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(9) Cell parameters were determined by a Siemens SMART CCD diffractometer. Crystal data: $C_{32}H_{16}BF_{24}NaO_2$, fw = 922.25, tetragonal, *P*4/*n*, $a = 13.8310(2)$ Å, $b = 13.8310(2)$ Å, $c = 9.8480(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 1883.89(5)$ Å^3, $Z = 2$, $D_{calcd} = 1.626$ Mg/m^3, $F(000) = 912$, 0.25 × 0.20 × 0.15 mm, θ range = 2.07−27.47°, 2165 independent reflections ($R_{int} = 0.0384$) out of 18 086 reflections collected, full-matrix least-squares on F^2, R1 = 0.0677, wR2 = 0.2162 [$I > 2\sigma(I)$], GOF on F^2 = 1.050.

10.1021/ic061162k CCC: $33.50

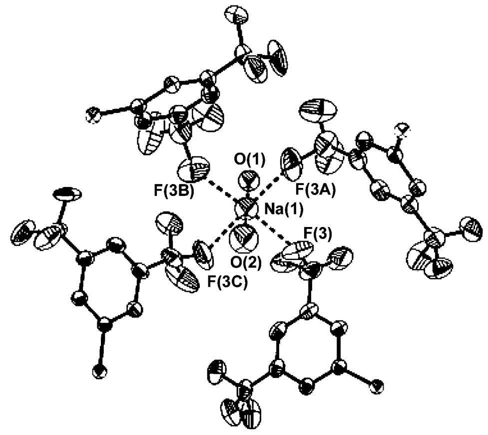


Figure 1. ORTEP plot of $[Na(H_2O)_2]BAr^F_4$.

from four different borate anions, allowing the sodium ion to reside in a hole surrounded by trifluoromethyl groups (a Teflon-coated cavity). Distances between the sodium ions and the fluorine atoms of the trifluoromethyl moieties are in the range of 2.44−2.68 Å, showing a close Na···F interaction. IR spectra of the sodium salt illustrate four distinct O−H stretchings at 3712, 3709, 3647, and 3630 cm^{-1}. When UB3LYP is adopted with the 3-21G* basis set, with incorporation of either natural population analysis (−0.1875) or electrostatic potential surface fitting (ChelpG ESP fit −0.3402) at the fluorine atom, the results of calculations estimate the vibrational frequencies of the O−H symmetric stretching to be 3802 and 3804 cm^{-1} and those of the O−H antisymmetric stretching to be 4047 and 4048 cm^{-1}, the trend of which is qualitatively consistent with the experimental results. The deviation of the current theoretical approach from the experimental results may plausibly be explained by negligence of the solvation effects in the gas-phase ab initio approach as well as the application of a rather small basis set due to the large molecular framework.

The crystal structure of $Li(H_2O)_4BAr^F_4$ reported by Golden and co-workers showed that the lithium ion was surrounded by four water molecules without any coordination of fluorine to the metal center.[10] This is quite different from the corresponding sodium species reported here. Presumably that is due to the smaller size and the higher hydration energy of the lithium ions.

Table 1. Polymerization of Vinyl Ethers and Styrenes

entry	monomer	PDI	conversion (%)
1	ethyl vinyl ether	5186 (3.3)	100
2	2,3-dihydrofuran	1200 (3.4)	27
3	isobutyl vinyl ether	12200 (3.4)	100
4	allyl vinyl ether	1100 (1.9)	50
5[c]	ethyl vinyl ether		
6[d]	ethyl vinyl ether		
7	*p*-methoxystyrene	16000 (2.8)	83
8	styrene		
9	*p*-chlorostyrene		

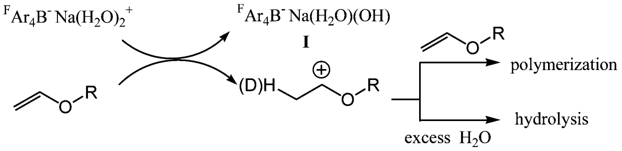
[a] $Na(H_2O)_2BAr^F_4$ (0.02 mmol), monomer (20 mmol), CH_2Cl_2 (5 mL), 24 h, 30 °C. [b] PDI = M_w/M_n. [c] Et_4NBArF_4 was used instead of the sodium salt. [d] Anhydrous $NaBAr^F_4$ was used. The anhydrous salt was prepared by heating $[Na(H_2O)_2]BAr^F_4$ at 150 °C under vacuum for 48 h.

Table 2. Anion Effect on the Polymerization of Vinyl Ether Catalyzed by Sodium Salts[a]

entry	salt	reaction time	yield (%)	PDI
1	$[Na(H_2O)_2]BAr^F_4$	10 min	25	15300 (3.75)
2	NaCl	24 h		
3	$NaBF_4$	24 h		
4	$NaPF_6$	24 h		
5[c]	$[Na(H_2O)_2]BAr^F_4$	24 h	trace	
6	$[Li(H_2O)_4]BAr^F_4$	10 min	<2	8100 (1.11)

[a] $M^+(BAr^F_4)^-$ (0.01 mmol), isobutyl vinyl ether (20 mmol) in CH_2Cl_2 (5 mL), at 30 °C. [b] Addition of 18-crown-6 to the solution of $[Na(H_2O)_2]BAr^F_4$ followed by the addition of vinyl ether.

Scheme 1. Polymerization and Hydrolysis of Vinyl Ether



Using $[Na(H_2O)_2]BAr^F_4$ as the catalyst, polymerization of vinyl ethers can be carried out under mild conditions (Table 1). In one of the typical reactions, a stirred solution of $[Na(H_2O)_2]BAr^F_4$ (0.02 mmol) with ethyl vinyl ether (20 mmol) in predried CH_2Cl_2 (5 mL) at 30 °C for 24 h produced poly(vinyl ether) quantitatively.[11] In an isotope-labeled experiment, it was found that deuterium was incorporated at the terminal of the polymer. Support of this is given by the intensity of *m*/*z* at M + 1 for the formula $H[CH_2CH(OEt)]_nOEt$. In addition, polymerization was not observed when anhydrous $NaBAr^F_4$ was used in an extremely dried solution (Table 1, entry 6). These observations clearly indicate that the reaction is initiated by a proton, not by the sodium ion, and is proceeded via a typical carbocation pathway, depicted in Scheme 1. As is also illustrated in Table 1, other vinyl ethers underwent polymerization smoothly under similar reaction conditions. On the other hand, when the reaction was carried out in an aqueous medium, ethyl vinyl ether was completely hydrolyzed into acetaldehyde and ethanol (see Scheme 1). When deuterated water was used, as expected, the deuterated acetaldehyde (DCH_2CHO) was formed. For the monomer of styrene derivatives, *p*-methoxystyrene did undergo polymerization but not the styrene itself or the chloro-substituted one. Apparently, the formation of a more stable carbocation intermediate is required for the process.

It has been well established that aqueous sodium chloride does not catalyze either polymerization or hydrolysis of vinyl ether. Apparently, the anion counterpart makes aqueous sodium ions with remarkably different properties. With an aim to screen the anion effect, as shown in Table 2, we found that polymerization of vinyl ether initiated by aqua sodium species does require the assistance of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. Other anions, such as the tetrafluoroborate or hexafluorophosphate used in this study, do not show a similar effect. It is also noticed that the formation of the sodium crown ether complex readily holds back the reaction (see entry 5 in Table 2).

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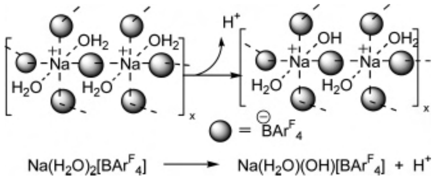
(11) Viscous liquid: $M_n = 5200$, $M_w/M_n = 3.3$. ^1H NMR: δ 3.6 (br, 1 H, OC*H*−), 3.48 (br, 2 H, OCH_2−), 1.70 (2 H, −CH_2−), 1.2 (t, 3 H, −CH_3). ^{13}C NMR: δ 74 (OCH_2), 64 (O*C*H−), 40 (−CH_2−), 16 (−CH_3).

As shown in the crystal structure, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate dihydrate consists of ions held together through the coordination of Na•••F. In a dichloromethane solution, this salt did not completely dissociate into free ions, with the formation of agglomeration instead.[12] From the dynamic light-scattering measurement, the average size of the agglomerated particles is in the range of 60−90 nm, indicating that coordination of Na•••F remains in the solution phase. Of course, the lipophilic interaction of the fluoro-substituted aryl group provides another important contribution to the agglomeration. Such a coordination environment makes the dissociation of a proton from the coordinated water feasible (Scheme 2). However, this interaction is readily interrupted by the addition of crown ether.

Upon exploring the unique acidic character of $[Na(H_2O)_2]BAr^F_4$ in the above study, we subsequently examined the possibility of using the lithium salt to carry out the acid-catalyzed reaction. However, the catalytic activity of the lithium salts was found to be much less than that of the sodium salt (Table 2, entry 6).

Scheme 2. Dissociation of Protons from the Aqua Sodium Salt



The comprehensive theoretical consideration of this system is currently under investigation. There are apparently many more interesting acid-catalyzed reactions following the present approach. We therefore believe that the results should raise a broad spectrum of interest in the field of catalysis and polymerization reaction.

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Supporting Information Available: Full details of the crystallographic data (CIF) for the sodium salt $[Na(H_2O)_2]BAr^F_4$, ^1H NMR spectral data of polymers, and the theoretical approach on vibrational frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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