Evaluation of Lewis Acidity of "Naked" Lithium Ion through Diels-Alder Reaction Catalyzed by Lithium TFPB in Nonpolar Organic Solvents

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The Diels-Alder reaction of cyclopentadiene with methyl vinyl ketone was remarkably promoted by anhydrous LiTFPB as a Lewis acid catalyst both in dichloromethane and in toluene. Experimental and computational investigations revealed the effects of solvent, hydrating water molecules, and counter anions on the Lewis acidity of the "naked" lithium ion.

The great affinity of lithium ion for organic compounds in gas phase[1] and the characteristic Lewis acidity of lithium ion in aprotic polar organic solvents[2] have been noteworthy among physical and organic chemists. In nonpolar organic solvents, however, there have been very few reports on the evaluation of the Lewis acidity of "naked" lithium ion with extremely small coordinative stabilization by solvent and counter anion because very few lithium salts are soluble in low donor-number solvents.[3]

Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (TFPB) ion[4] in Figure 1 is a weakly coordinating anion or a "superweak" anion[5] which can make various cations soluble in dichloromethane and toluene as a loose ion pair and promote electrophilic reactions with its "naked" counter cations.[6]

We demonstrate here the remarkable electrophilicity (Lewis acidity) of the dehydrated "naked" lithium ion ion-paired with TFPB ion even in toluene and dichloromethane whose catalytic activities are evaluated by monitoring the Diels-Alder reaction of cyclopentadiene with methyl vinyl ketone. Table 1 shows the relative rate constants and the product isomer ratio of the Diels-Alder reactions with various salts.[7]

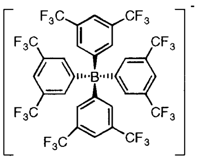
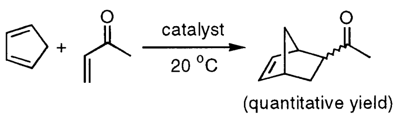


Figure 1. TFPB ion.



Scheme 1.

Table 1. Relative rate constants and product isomer ratio of the Diels-Alder reaction of cyclopentadiene with methyl vinyl ketone

Catalyst	mol%	Solvent	rel. k_{obs}	endo:exo
no catalyst[a,b]	0	toluene	1	80:20
$Li(H_2O)_nTFPB$, n<0.5	1	toluene	2000	94: 6
$Li(H_2O)_nNTf_2$, n<0.5	1	toluene	3.0	88:12
$Li(H_2O)_nCTf_3$, n=1	1	toluene	3.0	89:11
no catalyst	0	CH_2Cl_2	1.4	86:14
$Na(H_2O)_nTFPB$, n<0.5	9	CH_2Cl_2	20	92: 8
$Li(H_2O)_nTFPB$, n<0.5	9	CH_2Cl_2	>5700	93: 7
$Li(H_2O)_nTFPB$, n<0.5	1	CH_2Cl_2	140-780	94: 6
$Li(H_2O)_nTFPB$, n=4	1	CH_2Cl_2	4.2	88:12
$Li(H_2O)_nNTf_2$, n<0.5	1	CH_2Cl_2	4.2	88:12
$Li(H_2O)_nCTf_3$, n=1	1	CH_2Cl_2	4.2	89:11
no catalyst	0	Et_2O	0.46	80:20
$Li(H_2O)_nTFPB$, n<0.5	1	Et_2O	3.7	89:11

[a] $0.12\ mol{\cdot}l^{-1}$ of cyclopentadiene and $0.18\ mol{\cdot}l^{-1}$ of methyl vinyl ketone in 17.5 ml of toluene.
[b] k_{obs}(no cat.)$=8.3\times10^{-5}\ mol^{-1}{\cdot}dm^3{\cdot}s^{-1}$.

The catalytic activity of anhydrous LiTFPB is very high in toluene and in dichloromethane but low in diethyl ether; i.e., the rate constant with anhydrous LiTFPB is more than several hundred times of that without catalyst in toluene and dichloromethane but only eight times in diethyl ether. The activity of anhydrous LiTFPB is roughly half of $La(NTf_2)_3{\cdot}H_2O$, which is the strongest metal amide catalyst in the Diels-Alder reaction of cyclopentadiene and methyl vinyl ketone in dichloromethane, while that of LiTFPB tetrahydrate is comparable to those of $LiNTf_2$ and $LiCTf_3$.[3b] The activity of anhydrous NaTFPB is much lower than that of anhydrous LiTFPB, but the product ratio (92:8) is as high as that (93:7) of anhydrous LiTFPB. The endo:exo product ratio (94:6) with anhydrous LiTFPB in toluene and dichloromethane is higher than that (80:20) without catalyst and that (88:12) with the tetrahydrate in dichloromethane and that (89:11) with anhydrous LiTFPB in diethyl ether. The effect of counter anion, hydrating water molecules, and solvent is, thus, remarkable.

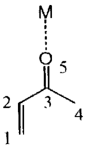
These experimental results disclosed that the intrinsic Lewis acidity of the "naked" lithium ion in solvents with low donor-number is very strong as in gas phase when it is loosely ion-paired with weakly coordinating anions with bulky substituents such as TFPB ion. The Lewis acidity of lithium ion, however, greatly decreases when lithium ion is strongly stabilized by coordinative solvation, by hydration, or by ion-pairing with smaller size anions.

The effect of water molecules on a large range of Lewis acidity of lithium ion from the "naked" lithium ion to hydrated lithium ions was computationally examined by using a simple model of methyl vinyl ketone complexed with "naked" and hydrated lithium ion. The optimized electronic structures of methyl vinyl ketone and their complexes with lithium and sodium ions as well as their hydrated complexes are obtained by RHF/6-31G* level calculations with SPARTAN V5.0 system.

Table 2 shows the energy levels of the LUMO+n involved in the frontier orbital interaction for the Diels-Alder reaction and the coefficient of LUMO+n on the carbonyl carbon of methyl vinyl ketone and its complexes with the "naked" lithium and sodium ions and their hydrates.

The LUMO+n energy level of the dienophile is remarkably lowered by complexing with lithium ion but not so much with hydrated lithium ions and sodium ion. The binding energy of the "naked" lithium ion is calculated to be 51.9 kcal/mol,

Table 2. Energy level and coefficient of LUMO+n and binding energy of methyl vinyl ketone and its complexes with lithium and sodium ions[a]



Metal ion	LUMO+n[b] level (eV)	Coefficient C_3^2	Binding energy (kcal/mol)
no cat.	0.1055	0.18695	
Li^+	-0.0806	0.50223	51.9
$Li^+(H_2O)_1$	-0.0595	0.42166	44.6
$Li^+(H_2O)_2$	-0.0418	0.36686	34.0
$Li^+(H_2O)_3$	-0.0288	0.30603	24.5
$Li^+(H_2O)_4$	-0.0199	0.29647	18.7
Na^+	-0.0481	0.30976	31.2

[a]Calculated by RHF/6-31G*.

[b]LUMO+n means the nth MO above the LUMO. n=1 with Li^+ and $Li^+(H_2O)_{1\text{-}4}$; n=3 with Na^+.

which gradually decreases when the hydration number increases. Similarly complexation with the "naked" lithium ion increases the coefficient on the carbonyl carbon which gradually becomes smaller when the coordination number of water increases. According to frontier orbital theory,[10] these computational results that the decreased HOMO(diene)-LUMO(dienophile) gap and the increased coefficients resulting in the increased reaction rate and product ratio, respectively, are well correlated with the experimental results; i.e., the Lewis acidity of anhydrous LiTFPB to affect the reaction rate and stereoselectivity is as remarkable as that of lihium ion in gas phase and stronger than those of LiTFPB tetrahydrate and anhydrous sodium TFPB.

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7 Lithium TFPB was isolated as tetrahydrate[8] colorless powder by recrystallization of a sticky oil obtained in a cation exchange reaction of Me_4NTFPB[4b] in diethyl ether with aqueous LiCl solution and dried under 5×10^{-2} mmHg at 100 °C for 3 h before using the Diels-Alder reaction. The number of coordinated water molecules was determined by ^1H-NMR by using $CHCl_3$ as an external standard. Dehydration at 80 °C under $1\text{-}3 \times 10^{-5}$ mmHg for 15 h gave anhydrous LiTFPB salt without decomposition. Lithium tris((trifluoromethyl)sulfonyl)methide ($LiCTf_3$) monohydrate was prepared by a similar exchange reaction of $KCTf_3$[9] with LiCl. Lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$) was prepared by a reaction of $HNTf_2$ with LiOH.[3b,3f] $LiCTf_3$ and $LiNTf_2$[3b,3f] were dehydrated similarly to LiTFPB. Dehydration of $LiNTf_2$ under $1\text{-}3 \times 10^{-5}$ mmHg for 15 h at 100 °C gave anhydrous $LiNTf_2$ without decomposition, while, after dehydration of $LiCTf_3$ monohydrate under the same conditions, more than 0.7 H_2O were still coordinated on $LiCTf_3$. The rate constants and product ratio were determined by gas chromatography as in the case of various metal imides catalysis reactions.[3b,3f] A typical kinetic experiment for the reaction with LiTFPB in dichloromethane: a dichloromethane (55 ml) solution of cyclopentadiene (9.74 mmol) containing internal standard decane (2.77 mmol) was mixed with methyl vinyl ketone (6.37 mmol) and 17.5 ml of this mixed solution was dropped into a two-neck flask containing LiTFPB (1 mol%). The Diels-Alder reaction was carried out at 20 °C under argon atmosphere with magnetic stirring. The concentration of water (9 ppm) in the dichloromethane solution was measured by a Karl-Fischer moisture titrator. In a given time a 0.1 ml solution was sampled, diluted four times, passed through a micro silica-gel column, and monitored by gas chromatography to determine the rate constant and the endo/exo product ratio.

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