Reactive N-Protonated Isocyanate Carbocation Stabilized by Bis(µ-hydroxo)divanadium(IV)-Substituted Polyoxometalate**

Kazuhiro Uehara, Keisuke Fukaya, and Noritaka Mizuno*

Polyoxometalates (POMs) are anionic nanosized metal oxide clusters that consist of early transition metals, and stimulate many current research activities in broad fields of science, such as catalysis, materials, and medicine, because their chemical properties, such as acidity and redox potential, can be finely tuned by constituent elements and countercations.^[1] Especially, acidic forms of POMs are active catalysts in various reactions, and some of them have been industrially used.^[1h,i] Spectroscopic data indicate that POMs induce unique activities by stabilizing reaction intermediates, such as onium and carbenium ions.^[1c,h,i,2] However, to the best of our knowledge, isolated unstable organic cationic intermediates stabilized by POMs that exhibit catalytic activity have never been reported, and only one structurally determined O-alkylated POM has been reported.^[3]

Carbocations play an important role as highly reactive intermediates for electrophilic C–C bond-forming reactions, such as Friedel–Crafts alkylation and acylation, Mukaiyama aldol reaction, and Tsuji–Trost reaction.^[4,5] Isolation of such reactive species is quite difficult because of the instability, and their existence is usually confirmed by NMR and IR spectroscopy.^[6] π Conjugation and hyperconjugation contribute to stabilization of the reactive species. Bulky conjugated bases of superacids, such as trifluoromethane sulfonate (CF₃SO₃⁻), tetrafluoroborate (BF₄⁻), and carborane, can also stabilize carbocations with electrostatic and hydrogenbonding interaction between the anionic and cationic moieties, thus enabling the determination of their structures by Xray crystallography.^[4c,f,7]

Isocyanates are reactive heterocumulenes that show a variety of reactivities for dehydration, deoxygenation, insertion, oligomerization, and polymerization.^[8] Especially the N-protonated isocyanate cation is energetically favorable by theoretical calculation,^[8] whereas the O-protonated one has been proposed as an intermediate for Friedel–Crafts

 [*] Dr. K. Uehara, Dr. K. Fukaya, Prof. Dr. N. Mizuno Department of Applied Chemistry, School of Engineering The University of Tokyo
 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
 E-mail: tmizuno@mail.ecc.u-tokyo.ac.jp

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acylation.^[8b] With regard to the isocyanate cations, their isolation and structural determination have never been realized. Herein, we report the formation and isolation of the putative "N-protonated phenyl isocyanate carbocation" by the reaction of a bis(μ -hydroxo)divanadium(IV)-substituted γ -Keggin-type POM, (TBA)₄[γ -SiV^{IV}₂W₁₀O₃₆(μ -OH)₄], with phenyl isocyanate.

The divanadium(IV)-substituted γ-Keggin-type POM was synthesized by the reaction of VOSO₄ with $K_8[\gamma$ -SiW₁₀O₃₆] in water, in which the pH value was adjusted to 4.8 with 0.1M acetate buffer. Addition of TBABr resulted in formation of reddish brown powders. Recrystallization from a mixed solvent of 1,2-dichloroethane and toluene gave dark brown crystals in 28% yield. The IR spectrum of 1 showed v(O-H)vibration bands at 3628 and 3566 cm⁻¹ and v(V=O) vibration bands at 1007 and 962 cm⁻¹ (see Figure S9 in the Supporting Information). Cold-spray ionization mass spectroscopy (CSI-MS) showed the parent signal centered at m/z = 3824.22, in agreement with $\{(TBA)_5H_4[SiV_2W_{10}O_{40}]\}^+$ (centered at m/z =3824.62; Figure S11). The ²⁹Si and ⁵¹V NMR spectra in CD₃CN did not exhibit any signals, suggesting the paramagnetic $d^{1}(V^{IV})$ - $d^{1}(V^{IV})$ high spin state in **1** (Figure S10). The magnetic susceptibility of 1 was 3.011(4) μ_B at 300 K, thus supporting the idea (Figure S24).

The molecular structure of 1 was successfully determined by single-crystal X-ray crystallography (see Figure 1a, and Tables S1 and S2 in the Supporting Information). Compound 1 was identified as $(TBA)_4[\gamma-SiV^{IV}_2W_{10}O_{36}(\mu-OH)_4]$, which contains a $V^{IV}_{2}(\mu$ -OH)₂ diamond core, in which the γ -Keggin framework was maintained by introduction of vanadium(IV) moieties. Four TBA cations per anion were observed. The bond-valence sum (BVS) values for O(113), O(114), O(126), and O(128) were 1.22, 1.21, 1.25, and 1.25, respectively, suggesting that these oxygen atoms are monoprotonated and two protons are generated on W-O-W bridging oxygen atoms (O(126) and O(128)) on introduction of two V^{IV} atoms (Table S3).^[9] The BVS values for the other bridging and terminal oxygen atoms were 1.70-2.06 and 1.59-2.00, respectively, suggesting that the valences are -2. The BVS values for Si (3.93), V (4.18 and 3.96), and W (5.64–6.42) suggest that the respective valences are +4, +4, and +6. All the data show formation of $(TBA)_4[\gamma-SiV_2^{IV}W_{10}O_{36}(\mu-OH)_4]$.

The V…V (3.101(5) Å), V=O (1.605(17) and 1.64(2) Å), and V–O(–V) (1.95(2)–2.01(2) Å) distances in **1** were similar to those in the vanadium(V) derivative, $(TBA)_4[\gamma$ -SiV^V₂W₁₀O₃₈(μ -OH)₂] **1**' (3.096(3), 1.631(14), and 1.577(14), and 1.957(13)–1.980(12) Å). On the other hand, the V…O(– Si) distances in **1** were 2.90(1) and 2.91(1) Å and much longer than those in **1**' (2.511(12) and 2.531(11) Å; Table S2).^[10] Therefore, the interaction between the diamond core and



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Figure 1. Thermal ellipsoid plots of a) $(TBA)_4[\gamma-SiV_2W_{10}O_{36}(\mu-OH)_4]$ **1**, and b) $(TBA)_4[\gamma-SiV_2W_{10}O_{38}(\mu-OH)_2(PhNHCO)_2]$ **2**, drawn at 50% probability level (TBA cations were omitted for clarity).

the $[\gamma$ -SiW₁₀O₃₆]^{8–} fragment in **1** is weaker than that in **1'**, probably because of the Jahn–Teller effect, which is characteristic of d^1 transition-metal complexes.^[11] The W(104)–O(126) and W(106)–O(128) distances were 2.163(13) and 2.185(13) Å, respectively, and thus longer than the others, because of monoprotonation at O(126) and O(128).

Next, the reactivity of 1 with phenyl isocyanate was investigated. Compound 1 was dissolved in a mixed solvent of acetone and 1,2-dichloroethane containing an excess amount of phenyl isocyanate. Keeping the reaction solution for one day gave dark brown crystals 2 in 71 % yield. The IR spectrum of **2** showed strong bands at 3335, 1736, 1597, and 1537 cm^{-1} , which are assignable to v(N-H),^[12] v(C=O), v(C=N), and v(C=C) vibration modes, respectively, suggesting the existence of a phenyl isocyanate moiety (Figure S12). The ¹H NMR spectrum of **2** was measured (Figure S13). Just after dissolution of 2 in CD₃CN, four broad signals of the phenyl isocyanate carbocation were observed at 8.77, 7.70, 7.40, and 7.03 ppm with the respective integration ratio of 1:2:2:1.^[14] Generally, the protons of alcohols have been observed in the range of 4-5 ppm, whereas those of imines and amides have been observed in the range of 8-9.5 ppm. For example, the NH protons of N,N'-diphenylurea were observed at 8.66 ppm in [D]₆DMSO.^[10] Therefore, the ¹H NMR signal at 8.77 ppm is assignable to the NH moiety and those at 7.70, 7.40, and 7.03 ppm are assignable to the o-, *m*-, and *p*-C₆H₅ moieties, respectively. In addition, the ${}^{13}C{H}$ NMR signals of CO (148.86 ppm)^[15] and Ph (130.27, 130.15, 126.76, and 119.38 ppm) were observed (Figure S14). The CSI-MS spectrum of 2 also showed the parent signal centered at m/z = 4062.27, in agreement with {(TBA)₅H₄[SiV₂W₁₀O₄₀-(C₆H₅NCO)₂]}⁺ (centered at m/z = 4062.70), thus supporting the idea (Figure S16). All these NMR and CSI-MS results support the existence of the phenylisocyanate moiety.

On the other hand, no signals were observed in ²⁹Si and ⁵¹V NMR spectra because of the paramagnetic nature of **2** (Figure S15).^[16] The magnetic susceptibility of **2** was 2.527(4) μ_B at 300 K. These results indicate the retention of valence of vanadium centers as +4 (Figure S25).

The molecular structure of 2 was successfully determined by single-crystal X-ray crystallography (see Figure 1b, and Figure S2 and Tables S1 and S2 in the Supporting Information). Four TBA cations per anion were observed. The BVS values for O(113) (1.30) and O(114) (1.25) indicate that these oxygen atoms are monoprotonated. No proton was observed on O(126) and O(128), respectively, thus suggesting the reaction of two protons on O(126) and O(128) in 1 with phenyl isocyanate (Table S4). The BVS values of the other bridging and terminal oxygen atoms were 1.73-2.09 and 1.46-1.86, respectively, suggesting that the valences of these oxygen atoms are -2. Therefore, the valences of O(126) and O(128) in 2 were decreased to -2 by the deprotonation of 1. W(104)-O(126) The (2.010(13) Å), W(110)-O(126) (1.873(13) Å), W(106)–O(128) (1.996(12) Å), and W(112)– O(128) (1.882(12) Å) distances were shortened, thus supporting the idea. The N(11)-O(128) and N(21)-O(126) distances in 2 were 2.885 and 2.839 Å, respectively, suggesting the hydrogen-bonding interaction between the carbocation and POM, which would stabilize the carbocations.

We next focused on the organic moieties depicted in Figure 2, and Figure S3 in the Supporting Information. Phenyl isocyanate is a planar molecule as a result of π conjugation of the C(Ph)–N=C moiety. When protonation takes place at the O atom of the phenyl isocyanate, the π conjugation is retained and those atoms can keep linear conformation. On the other hand, when protonation takes place at the N atom, the π conjugation collapses and the C(Ph)–NH–C⁺=O moiety becomes bent because of sp³ hybridization. Those



Figure 2. Representative molecular orbitals illustrating interaction between the N-protonated phenyl isocyanate and POM in **2** (isosurface value 0.01), a) $\alpha(212)$ orbital, b) $\alpha(212)$ orbital with emphasis on cationic moiety, c) $\alpha(210)$ orbital, and d) $\alpha(210)$ orbital with emphasis on cationic moiety.^[17]

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phenomena were confirmed by DFT calculation (Table S7 and Figure S8).^[18] The C(11)–N(11) distance (1.41(2) Å) and C(11)-N(11)-C(17) angle (125.9(18)°) of the carbocation in **2** show the single bond and bent characters, respectively. The IR band of N–H stretching vibration and ¹H NMR signal of NH of the N-protonated phenylisocyanate carbocation were observed at 3335 cm⁻¹ and 8.77 ppm, respectively. The DFT calculation showed that the N-protonated one (Figure S8). All these results show that protonation takes place at the N atom of the phenyl isocyanate. Two protons at O(126) and O(128) in **1** probably transfer to the N atoms of phenyl isocyanates in close proximity to O(126) and O(128) in **2**.

The C(17)–O(11) and C(17)–N(11) distances were 1.20(3) and 1.33(3) Å, respectively, exhibiting double bond characters, whereas the C(17)-O(124) distance was 1.44(3) Å and thus much longer than the C(17)-O(11) distance. DFT calculation of the anionic part of 2 also supports the hypothesis of the interaction between the N-protonated phenyl isocyanate cation and POM. The representative orbitals $\alpha(212)$ and $\alpha(210)$ prove that the C(17)-O(124) bond mainly consists of the polar π interaction (electrostatic attraction; coefficients of p_v orbitals (0.035 for C(17) and 0.113 for O(124)) with slight contribution of the σ bond (coefficients of p_x orbitals (0.047 for C(17) and -0.046 for O(124)).^[19] The Mulliken charge of the carbonyl moiety (0.809) in the N-protonated phenyl isocyanate cation was almost the same as that without the POM (0.827), thus supporting the idea that the interaction between O(124) and C(17) is weak (Table S6). N(11)-C(17)-O(124), O(11)-C(17)-O(124) and O(11)-C(17)-N(11) angles were 111.5(18), 117(2), and 132(2)°, respectively, and the sum of these angles was approximately 360°. The W(103)-O(124) and W(106)-O-(124) distances were 2.101(13) and 2.118(13) Å, respectively, and longer than those of the other W-O(-W) bonds (1.855(15)-2.010(13) Å) These facts show that N(11), C(11), O(11), and C(17) atoms are placed in the same plane by the sp² hybridization. In addition, N(11)...O(128) and N(21)...O-(126) distances were 2.885 and 2.839 Å, respectively, suggesting the presence of the hydrogen-bonding interaction, which would stabilize the carbocations. All the results lead to the conclusion that compound 2 is assignable to $(TBA)_4[\gamma$ - $SiV_{2}^{IV}W_{10}O_{38}(\mu-OH)_2(PhNHCO)_2]$, which is the first example of isolation and stabilization of the N-protonated phenyl isocyanate carbocation by using the bulky POM.

The reaction of **1** with phenyl isocyanate at room temperature for about three months produced 1,3,5-triphenylisocyanurate **3**^[20] and **2**. In addition, compound **1** catalyzed cyclotrimerization of phenyl isocyanate to form **3** in 39% yield at 333 K. Compound **2** catalyzed the same reaction at the lower temperature of 323 K to form **3** and 2-(phenylimino)-1,3,5triphenylhexahydro-*s*-triazine-4,6-dione **4**^[21] in 49% and 25% yields, respectively (moles of products **3** + **4**/moles of catalyst = 3.3; see Scheme 1, and Figures S17–S23 in the Supporting Information). All these results show that the N-protonated phenyl isocyanate in **2** is the intermediate for the catalysis.^[22]

In conclusion, the novel bis(μ -hydroxo)divanadium(IV)-substituted POM, (TBA)₄[γ -SiV^{IV}₂W₁₀O₃₆(μ -OH)₄] **1** was



Scheme 1. Cyclotrimerization of phenyl isocyanate catalyzed by **2** (yields in parentheses are those of isolated products). *N*,*N*'-diphenylurea would be formed by hydration and decomposition of phenyl isocyanate.^[8c]

synthesized and fully characterized by IR and CSI-MS spectroscopy and X-ray crystallography. Two protons at W– O–W bridging oxygen reacted with two phenyl isocyanate molecules to form $(TBA)_4[\gamma-SiV^{IV}_2W_{10}O_{38}(\mu-OH)_2-(PhNHCO)_2]$ **2** with the theoretically proposed N-protonated phenyl isocyanate carbocations. The cations weakly interacted with the bridging oxygen atoms of the POM through the polar π interaction mainly contributing from the POM with small contribution of the σ bond as well as the hydrogenbonding interaction. Compound **2** catalyzed the cyclotrime-rization of phenyl isocyanate to produce 1,3,5-triphenylisocyanurate **3** and 2-(phenylimino)-1,3,5-triphenylhexahydro-*s*-triazine-4,6-dione **4**.

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the strong asymmetric and very weak symmetric N–H vibration bands appear at 3410 and 3412 cm⁻¹, respectively (without any corrections). Therefore, the band observed at 3335 cm⁻¹ in **2** is assigned to the N–H stretching vibration mode.

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K. Uehara, K. Fukaya, N. Mizuno* _____

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Reactive N-Protonated Isocyanate Carbocation Stabilized by Bis(µhydroxo)divanadium(IV)-Substituted Polyoxometalate



O- or N-protonated? The bis(μ -hydroxo)divanadium(IV)-substituted γ -Keggintype polyoxometalate (see picture, left) (TBA)₄[γ -SiV^{IV}₂W₁₀O₃₆(μ -OH)₄] (TBA = tetra(*n*-butyl)ammonium) was synthesized and characterized by X-ray crystallography. Its reaction with phenyl isocyanate gave (TBA)₄[γ -SiV^{IV}₂W₁₀O₃₈(μ -OH)₂-(PhNHCO)₂], which contains two N-protonated phenyl isocyanate carbocations and catalyzes the cyclotrimerization of phenyl isocyanate.