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Induced-Fitting and Polarization of Bromine Molecule in an Electrophilic Inorganic Molecular Cavity and Its Bromination Reactivity

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Abstract: Dodecavanadate, $[V_{12}O_{32}]^{4-}$ (**V12**), possesses a 4.4 Å cavity entrance, and the cavity shows unique electrophilicity. Due to the high polarizability, Br₂ was inserted into **V12**, inducing the inversion of one of the VO₅ square pyramids to form $[V_{12}O_{32}(Br_2)]^{4-}$ (**V12(Br2)**). The inserted Br₂ molecule was polarized and showed a peak at 185 cm⁻¹ in the IR spectrum. The reaction of **V12(Br2)** and toluene yielded bromination of toluene at the ring, showing the electrophilicity of the inserted Br₂ molecule. Compound **V12(Br2)** also reacted with propane, *n*-butane, and *n*-pentane to give brominated alkanes. Bromination with **V12(Br2)** showed high selectivity for 3-bromopentane (64%) among the monobromopentane products and preferred *threo* isomer among 2-,3-dibromobutane and 2,3-dibromopenane. The unique inorganic cavity traps Br₂ leading the polarization of the diatomic molecule. Due to its new reaction field, the trapped Br₂ shows selective functionalization of alkanes.

Alkanes are the major constituents of natural gas and oil. The chemical inertness of the sp³ C–H bond, which has high bond dissociation energy and low polarity, makes it difficult to use alkanes as the carbon source of several chemical products. Although the conversion from sp³ C–H to C–X (X = C, N, O, S, Se, halogen) bond has been reported by several energetic researchers, an innovative methodology for the direct conversion of abundant and simple alkanes into value-added products are strongly required from practical and fundamental points of view.^[1–3]

Organobromine compounds are versatile intermediates.^[4] To establish a direct bromination reaction of alkanes is important, because it provides a useful scaffold for the introduction of variety

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of substituent on alkane framework. The direct conversion of alkane to bromoalkane is usually carried out by free radical processes.^[5] On the other hand, the polarized bromination of alkanes was reported by Olah and coworkers.^[6] The cationic Br^{δ+}, acting as an electrophilic reagent, reacts with the alkane via a pentacoordinate carbonium intermediate.^[6] Particularly, polarized halogenation of methane is expected to be highly selective for monohalogenated methane.^[7] because the halogen atom increasingly dominates the donating ability of the σ (C–H) bond.^[7] In addition, the size of bromine affects the formation of monohalogenated methane unlike that of chlorine.^[8–11] To prepare polarized Br₂, the creation of a reaction field with a pair of Lewis acid and base in the appropriate space is required.^[12-14]

Polyoxometalates are a large family of early transition metal oxide cluster anions that exhibit well-defined (sub)nano-sized molecular structures.^[15-19] Keplerate-type polyoxometalates possess pore-like voids with a diameter ca. 3.6 Å on their surface through which organic molecules can enter.^[20,21] The bowl-type structure of dodecavanadate ([V₁₂O₃₂]⁴⁻, V12) is composed of twelve VO₅ square pyramids and has a cavity diameter of 4.4 Å.^[22] The interior of the guest-occupied V12 is relatively cationic owing to high-valent and coordinatively unsaturated vanadium atoms to stabilize an electron-rich group or anion, while the cavity entrance is relatively anionic owing to the eight oxygen atoms.^[23-26] Among the halogen atoms, bromine fits the V12 cavity the best.^[26] This specific feature of V12 inspired the idea of preparing an polarized Br₂ by inserting Br₂ into the V12 bowl and using this polarized Br₂ as the electrophilic reagent for alkane bromination.

Among several neutral-molecule-occupied V12, tetra-nbutyl ammonium salts of V12 with 1,2-dichloroethane (DCE) ({n-Bu₄N₄[V₁₂O₃₂(DCE)], V12(DCE)) show high crystallinity.^[28] Single crystals of V12(DCE) in a 50 mL eggplant flask were exposed to 1 equiv of Br₂ gas with respect to V12(DCE). Fortunately, the crystallinity remains high after the disappearance of the brown color of Br₂, and the product is suitable for singlecrystal X-ray analysis (Figure 1, Table S1). The V12 crystal structure is maintained and one DCE is inserted into the V12 bowl as a guest molecule. The arrangement of tetra-n-butyl ammonium cations are almost the same as that in the original single crystals. The crystalline DCE near the rim of the V12 bowl is partly substituted by Br₂. The calculated occupancy of Br₂ from crystal analysis (39%) is identical to that from elemental analysis. The Br-Br bond length is 2.31 Å, and the distance between a bromine atom and the nearest-neighbor oxygen atom of V12 is 2.57 Å, showing the presence of a halogen bond interaction (Figure 1).^[29] There are some reports of single-crystal analysis of samples containing Br₂.^[30-34]

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Figure 1. Anion structures of (a) **V12-free** and (b) **V12(DCE)** with adsorbed Br₂ based on X-ray crystallographic analysis. (c) Schematic representation of the possible **V12(Br2)** structure and Br₂ polarization. Orange and red square pyramids represent VO₅ units. Orange, red, black, green, and brown balls represent vanadium, oxygen, carbon, chlorine, and bromine atoms, respectively. Hydrogen atoms are omitted for clarity. The dotted line represent balogen bond interaction.

The X-ray analysis reveals that DCE effectively caps the cavity and it prevents insertion of Br_2 in the cavity. After removal of the crystalline solvents, Br_2 adsorption on **V12(DCE)** was carried out in a glass vessel of the prescribed volume with a greaseless valve (Figure S1). With increasing pressure of Br_2 gas, the amount of adsorbed Br_2 gradually increases, and 1 mol/mol Br_2 to **V12(DCE)** is adsorbed at 2.5 kPa of Br_2 gas (Figure S2).

For the insertion of Br₂ into the V12 structure, tetra-n-butyl ammonium salts of guest-free V12 (V12-free) were prepared (Figure 1).^[35] In the previous work, it is revealed that one of the VO₅ square pyramids at the bottom of the bowl was flipped by removing a guest molecule, and that the flipped VO5 unit was retrieved by re-inserting the guest molecule. These structural transformations were observed by monitoring the 850 cm⁻¹ peak due to the V-O stretching vibration of the bottom part of V12 by IR. The Br₂ adsorption isotherms for V12-free show that the amount of Br_2 adsorbed on V12-free at 2.5 kPa (ca. 2 mol/mol) is larger by 1 mol/mol than that on V12(DCE) (Figure S2). The difference between V12(DCE) and V12-free is the presence or absence of a DCE guest. Therefore, the additional adsorption of Br₂ on V12-free indicates the insertion of Br₂ as a guest of V12. To clarify the insertion of Br2 into the V12 structure, in-situ IR spectra were measured (Figure 2). The intensity of the peak at around 850 cm⁻¹ due to V-O stretching vibration of V12-free is low compared with that of the guest-occupied V12, and the peak at 952 cm⁻¹ probably due to the terminal V–O stretching vibration of flipped VO₅ is observed only in the spectrum of V12-free. Under 0.6 kPa of Br2 gas at 20 °C, the peak at 856 cm⁻¹ increases, while that at 952 cm⁻¹ decreases, with time, suggesting the insertion of a guest into V12. After 20 min, the peak at 952 cm⁻¹ almost disappears. Upon evacuation of Br2 gas from the vessel, a new



Figure 2. IR spectra of V12-free coated onto a Si disk (a) before and (b) after exposure to 0.6 kPa of Br_2 gas. The spectrum in red is measured after evacuation of excess Br_2 gas. The insertion is represented by the difference spectrum between spectrum (b) and the spectrum in red.

peak at 185 cm⁻¹ appears. This peak is not observed when the experiment is performed with V12(DCE) instead of V12-free. The peak at 185 cm⁻¹ observed with V12-free, disappears upon reexposure to 0.6 kPa of Br2 gas and reappears upon evacuation of the gas. These results indicate that dodecavanadate with a Br₂ molecule as a guest ([V12O32(Br2)]4-, V12(Br2)) is obtained by exposure of V12- free to Br₂ (Figure 1). The peak at 185 cm⁻¹ is due to the polarized Br₂.^[36] Density functional theory (DFT) calculation supports the spectrum change. The energy of the optimized structure of V12(Br2) is 5.6 kJ/mol lower than the sum of the energy of V12-free and free Br₂. The Mulliken charge of outer Br atom is higher than the other, showing the polarization of Br2. The vibrational frequencies of calculated V12(Br2) is identical to the guest-occupied V12 in the main region of V-O stretching vibrations They also show the peak due to Br-Br in the lower region of V-O stretching vibrations. The cause of the observation of an IR-inactive Br-Br stretching band is the polarization of Br₂ molecule in the cavity: the arrangement of vanadium atoms in the cavity make the one of the Br atom partially electronegative and oxygen atoms at the entrance make the outer Br atom electropositive. The disappearance of the peak at 185 cm⁻¹ in the presence of excess Br₂ is probably caused by intermolecular bromine interaction, which reduces the dipole moment of the guest. In the previous work, molecules with low- or non-polarity, such as CO, O₂, N₂, H₂, and CH₄ under 0.1 kPa, showed no interaction with the inside of V12.[35] The reason Br₂ can be inserted to V12 is the high polarizability of Br₂. The insertion rate of Br₂ into V12 was determined by monitoring the peak at 856 cm⁻¹ (Figure S4). The rates at 0.6 kPa of Br_2 gas at -5, 10, and 20 °C are 0.025, 0.043, and 0.10 s⁻¹, respectively, which yield an activation energy of 35 kJ/mol.

Quantitative reaction between **V12-free** and Br₂ gas was carried out (Figure S5). The gas-phase UV-visible spectrum of 50 μ mol of Br₂ shows a peak at 415 nm. 50 μ mol of Br₂ exist as gas in the 9.8 mL cell at 20 °C. While the condensation of Br₂ was

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observed in the cell at -10 °C, 20 µmol of Br₂ existed as gas with showing 0.40 absorbance at 415 nm with an optical path length of 1 cm.^[37] On the other hand, in the presence of 50 µmol of the solid of V12-free, no condensation of Br₂ was observed at -10 °C, showing the adsorption of Br₂ by V12.^[37] The absorption of the gas phase UV spectrum at 415 nm was below 0.01, suggesting the adsorption of over 90% of Br₂ by V12 at -10 °C. Elemental and IR analyses confirm the quantitative insertion of Br₂ to form V12(Br2). The X-ray absorption fine structure (XAFS) measurements also support the formation of V12(Br2). The Fourier transform magnitude of radial distribution functions for the vanadium K-edge extended XAFS (EXAFS) spectra of bromideoccupied V12 (V12(Br) and V12-free substantially reflects the distribution of the bond distances in their crystal structures (Figure S6). The result of V12(Br2) is similar to that of V12(Br) rather than that of V12-free. The peak intensity ratio of second to third peaks of V-O bonds of V12(Br) and V12(Br2) are larger than that of V12-free. The fourth and fifth peaks of V-V distances of V12(Br) and V12(Br2) are slightly shorter than those of V12-free. The bromine K-edge EXAFS spectrum suggests a Br-Br distance of 2.33 Å, which is slightly longer than that in gas-phase Br₂ (2.28 Å, Figure S7).[38]

Release of Br₂ from V12(Br2) was investigated. ⁵¹V NMR spectra of V12(Br2) in acetone or *N*,*N*-dimethylformamide is identical to that of V12-free, suggesting the weak affinity between Br₂ and the cavity of V12.^[27] Thermogravimetry analysis (TGA) of V12(Br2) shows 6.35% weight loss by 80 °C (Figure S8). This value is 10% lower than the calculated value of the release of Br₂ from V12(Br₂) (7.09%). Due to the weak affinity, part of Br₂ was desorbed from V12(Br2) during the preparation under an ambient condition. IR spectrum of the sample after heating to 80 °C with TGA, shows the structure conversion to V12-free. This structure conversion also occurred with vacuum treatment of V12(Br2) at 25 °C, and the released Br₂ was collected in a cold trap.

To confirm the polarization of Br_2 in **V12(Br2)**, the reaction with toluene was investigated (Scheme 1). The suspension of 50 µmol of **V12(Br2)** in 2 mL of toluene gives 33 µmol of ringbrominated products as the main products. Addition of liquid Br_2 to toluene produced benzyl bromide as the main product via a radical reaction mechanism. The pretreated **V12(DCE)** exposed to 1 equiv of Br_2 gas (**V12(DCE)-Br2**) gave benzyl bromide as the main product. These results indicate that Br_2 inserted into **V12** acts as an electrophilic reagent, while the external Br_2 participates in a radical reaction.

After the reaction V12(Br2), the solid was filtered out. The IR spectrum shows that the V12 framework is maintained during

Scheme 1. Bromination of toluene. The reaction is carried out with 50 μmol of bromine source in 2 mL of toluene at 25 °C for 15 h..



the reaction (Figure S9). The strong intensity at 850 cm⁻¹ shows the insertion of the guest moiety into **V12**. The ⁵¹V NMR spectrum of the sample in acetone after the reaction shows peaks at –583, –587, and –599 ppm due to $[V_{12}O_{32}(Br)]^{5-}$. (Figure S10). With time, new peaks due to $[HV_{12}O_{32}(Br)]^{4-}$ increases, suggesting that the structure conversion to $[HV_{12}O_{32}(Br)]^{4-}$ with the presence of proton.^[39,40] On the other hand, when **V12(Br2)** is dissolved in acetone, ⁵¹V NMR spectrum shows the removal of Br₂ to form **V12-free**. These results suggest that HBr-occupied **V12** is produced by the bromination with **V12(Br2)**.

The bromination of *n*-pentane with V12(Br2), V12(DCE)-Br2, and Br₂ gives monobromopentane and dibromopentane (Table S2). Because of the difficulty of separating bromoalkane isomers, the development of a selective bromination reaction is significant.^[41] The selectivity for the brominated products with V12(Br2) is different from those of V12(DCE)-Br2 and Br₂(Figure 3). 3,3-Dibromopentane, which is selectively obtained by the reaction of *n*-pentane with {*n*-Bu₄N}Br₃, is observed in all cases. As the bromination products from tetra-*n*-butylammonium, 0.7 µmol of dibromobutane is detected with V12(Br2). The contributions of the inserted and external Br₂ in the V12 structure were evaluated by considering the selectivity for specific bromination products with V12(Br2) and V12(DCE)-Br2 as discussed below.

With V12(Br2), the ratio of 3-bromopentane (64%) among the monobromopentane products is higher than those with V12(DCE)-Br2 (21%). To explain this selectivity, the bromination of monobromopentane compounds was investigated (Table S3). After 15 h of competitive bromination of a 50 μ mol mixture of 2and 3-bromopentane (55:45) with 50 μ mol of V12(Br2) in perfluorohexane, 30 μ mol of monobromopentane remains with the ratio of 2-bromopentane and 3-bromopentane being 22:78. In the case of V12(DCE)-Br2, 27 μ mol of monobromopentane remains and the ratio of 2-bromopentane and 3-bromopentane is same as that before the reaction. These results suggest that the high ratio of the obtained 3-bromopentane with V12(Br2), is due to the consumption of 2-bromopentane formed during the reaction. The bromination of 2- and 3-bromopentane with



Figure 3. Selectivity for brominated products in the reaction of *n*-pentane with a bromine source. The reaction is carried out with 50 μ mol of bromine source in 2 mL of *n*-pentane at 25 °C for 15 h.

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V12(Br2) gives 2,3-dibromopentane and 1,2-dibromopentane (Table S3). The diastereoselectivity of 2,3-dibromopentane obtained with **V12(Br2)** and the mixture of 2- and 3-bromopentane is unique, showing 83% of the *threo* isomer.^[42] In the radical mechanism with **V12(DCE)-Br2**, 6.7 µmol of 2,3-dibromopentane, with the ratio of the *threo* and *erythro* isomers being 30:70. The reactivity of 1-bromopentane with **V12(Br2)** is low and no dibromopentanes were obtained. Going back to the bromination of pentane, the distribution of the selectivity for *threo*-2,3-dibromopentane is 44%. This values indicate that ca. 50% of Br₂ inserted into **V12** and ca. 50% of Br₂ external to **V12** reacted. The reaction of **V12(Br2)** with 2-methylbutane gave trace amount of monobrominated products and 1.1 µmol of dibrominated products, while Br₂ gave 2-bromo-2-methylbutane as a main product.

In addition, **V12(Br2)** reacted with *n*-butane and propane to give 2-bromobutane 2,3-dibromobutane, and 1,2-dibromopropane, and 2-bromopropane and 1,2-dibromopropane, respectively (Table S2). The diastereoselectivity of 2,3-dibromobutane is also unique, showing 70% of the *threo* isomer. The reactivity of butane and propane with **V12(Br2)** is higher than that of pentane due to the size of alkanes.^[43]

In conclusion, by the reaction of V12-free with Br2, one of the VO₅ square pyramids flipped to accept the inserted Br₂. Owing to the electrophilicity of the interior of the V12 bowl, the inserted Br2 was polarized, as detected by IR spectroscopy. To the best of our knowledge, this is the first reported spectroscopic evidence of polarized Br₂. The polarized Br₂ in V12 acted as an electrophilic reagent and showed unique reactivity toward pentane, which is clearly different from the radical reaction of free Br₂. In this demonstration, tetra-n-butyl ammonium salts of V12 without pores in the solid was used, and owing to the flexibility of the nbutyl chains, Br₂ and the substrate reached the active site of the opened mouse of V12. To improve the reactivity, 3-dimensional structure control with pore is desired, and for the application of more difficult methane bromination, the C-H activation site should be composited near the V12 bowl. Thus, the well-defined electrophilic molecule-sized cavity polarizes Br₂. The production of a reaction field at the molecular level gives definite spectroscopic data, which is essential to explaining the reaction mechanism, and leads to further development of a reaction field.

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To accept the insertion of Br_2 , the bowl type structure of dodecavanadate was rearranged. Due to the unique electrophilic feature of the bowl inside, Br_2 was polarized to be observed by IR. Polarized Br_2 in dodecavanadate bowl, acted as an electrophilic reagent to achieve selective bromination of propane, *n*-butane, and *n*-pentane.