Kurbah and Clovis *Discover Chemistry* (2026) 3:91
https://doi.org/10.1007/s44371-026-00557-0

Discover Chemistry

RESEARCH Open Access

Hydrazone ligated–vanadium(V) complex: catalytic oxidative bromination of organic substrates promoted by Brønsted acid or Lewis acid

Sunshine Dominic Kurbah[1*] and Ndege Simisi Clovis[2]

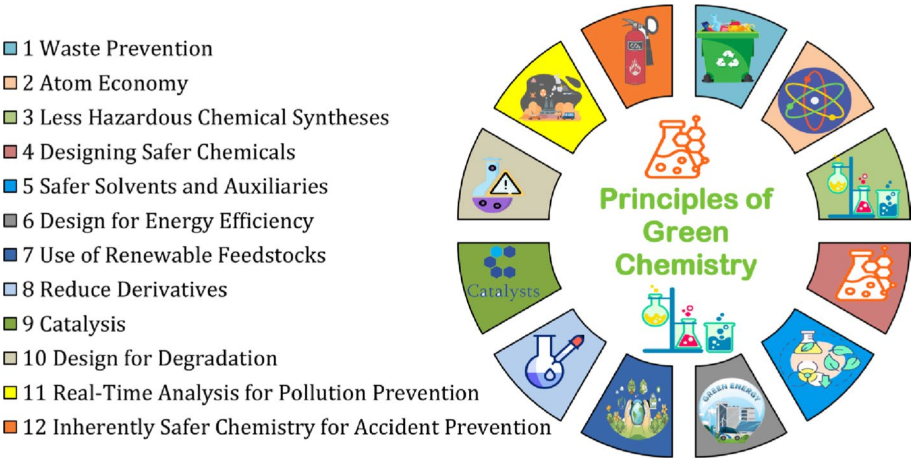
*Correspondence:
Sunshine Dominic Kurbah
sunshinekurbah@yahoo.com
[1]Department of Chemistry, Pandit Deendayal Upadhyaya Adarsha Mahavidyalaya, Eraligool, Sribhumi 788723, Assam, India
[2]Department of Chemistry, Faculty of Science and Technology, University of Kinshasa, Kinshasa, B.P.190, Kinshasa XI, Democratic Republic of Congo

Abstract
Vanadium(V) complex was prepared by reaction of vanadium acetylacetonate with hydrazone ligand. The complex was characterized by IR, ^{1}H NMR and UV-Visible spectroscopy. The structure of the complex was confirmed by single crystal X-ray crystallography. The complex shows biomimetic catalytic activity similar to that of haloperoxidases enzyme and brominate various organic substrates efficiently in presence of bromide salt, Lewis acid, or Brønsted acid. It was shown that using aluminium halide as a Lewis acid instead of a Brønsted acid produced a more workable approach for oxidative bromination reactions. In our current studies we observed that oxidative bromination reaction of ketones yielded only *α*-bromination products. It was discovered that $AlBr_3$ functioned as a Lewis acid and a source of bromide to easily initiate the bromination reactions.

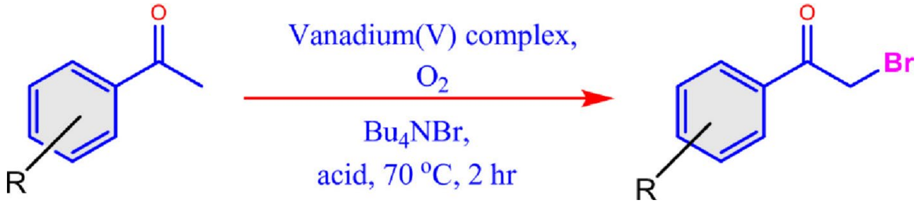
Keywords Catalysis, Oxidative bromination, Vanadium, Brønsted acid, Lewis acid

1 Introduction

The terms "green chemistry" and "sustainable chemistry" which are somewhat different but similar, have been gaining attraction in the scientific community [1–3]. The Organisation for Economic Cooperation and Development (OECD), states that "sustainable chemistry" is a scientific idea that aims to increase the effectiveness of using natural resources to satisfy human demand for chemical goods and services [4–8]. Sustainable chemistry encompasses the development, manufacturing, and use of safe, secure, efficient, and environmentally friendly chemical processes and products. According to sustainable chemistry, the cost-benefit ratio of any chemical process must consider the sustainable risk associated; lowering the risk allows for the assurance of a high standard of living, the decrease of environmental damage, and economic advancement [9–13]. Green Chemistry, on the other hand, emphasizes on developing chemical processes that minimize pollution and are beneficial for the environment and human health. Green Chemistry, according to Anastas and Warner, is the application of a set of principles that



Scheme 1 The use of a set of principles that reduces wastes and hazardous substances in chemical synthesis



Scheme 2 Schematic diagram showing the oxidative bromination of organic substrate using vanadium(V) complex

minimizes or eliminates the use or production of hazardous chemical in the design, production, and usage of chemical products [14, 15].

In green and sustainable chemistry, catalysis is very useful especially whenever recycling of the catalyst is required. However, much metal catalysis frequently used either a poisonous or precious metals, therefore it is important to select some metals such as iron or vanadium which are easily available, less expensive and generally non-toxic in nature [16–20]. Vanadium is one of the most abundant elements with many accessible oxidation states and plays significant roles in medical and biochemistry, and the coordination chemistry of vanadium has led to many applications in both heterogeneous and homogeneous catalysis and synthesis [21–24]. In our previous work, we have achieved the catalytic oxidative bromination by using vanadium complexes, hydrogen peroxide, perchloric acid and KBr under aerobic condition. However, these methods required a stoichiometric concentration of a potent protic acid [25]. Therefore, our research has led us to create a more adaptable and greener approach for bromination reactions (Scheme 1). Hence, herein we report the synthesis, characterization and catalytic oxidative bromination of organic substrates using vanadium complex as a catalyst, a bromide salt, and either a Lewis acid or a Brønsted acid (Scheme 2).

2 Experimental

2.1 Chemicals and physical measurements

Solvents and reagent were used as received. The ligand was synthesized following the procedure reported in the literature [26]. Other chemicals such as vanadium acetylacetonate, salicylaldehyde, phenol red, 5-bromo salicylaldehyde, 2-nitro phenol, ethyl salicylate, acetophenone, 2-hydroxy acetophenone, *p*-methoxy-acetophenone, 4-methyl-2-hydroxyacetophenone, 5-methyl-2-hydroxy-acetophenone, *p*-methyl-acetophenone, *m*-methyl-acetophenone and other metal salts were purchased from Sigma Aldrich, HiMedia and were used as received without any further purification. All operations were carried out under aerobic conditions. The ^{1}H NMR and ^{13}C NMR spectra were recorded on AMX-400 MHz and 100 MHz in DMSO-d_6 solution using tetramethylsilane as internal standard.

2.2 Single X-ray crystallography

Single crystal X-ray data of the complex were collected using Xcalibur, Eos, Gemini diffractometer equipped with a monochromated Mo K radiation ((λ = 0.71073 Å). The CrysAlis PRO; Agilent, 2013 software packages were used for data collection and reduction. The intensity data were corrected using semi empirical absorption method. In all cases absorption corrections based on multiscan using SADABS software were applied [27].The crystal structure was solved and refined using SHELXL-2014 [28]. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were place at a calculated position and refined in the final refinement using riding model. Crystallographic data of the complex have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-2441189 (deposit@ccdc.cam.ac.uk, https://www.ccdc.cam.ac.uk).

2.3 Preparation of vanadium(V) complex

Hydrazone ligand (0.24 g, 1 mmol) was dissolved in 20 mL of methanol and stirred for few minute and vanadyl acetylacetonate (0.27 g, 1 mmol) was added and stirred for another 30 min. The reaction mixture was then refluxed at 70 °C for 45 min and cooled to room temperature followed by addition of sodium carbonate (1 mmol) and stirred at room temperature for 30 min. The resulting solution yielded a light brown precipitate. The precipitate was collected, dried at room temperature and kept it in the desiccator. Colour: light brown; M.p: >320 °C. Analysis found % for $C_{26}H_{34}N_6Na_2O_{16}V_2$: C, 37.40; H, 4.10; N, 10.00; V, 12.20. Calculated % for $C_{26}H_{34}N_6Na_2O_{16}V_2$: C, 37.42; H, 4.11; N, 10.07; V, 12.21. IR data (cm^{-1} KBr): 3485 ν(–NH + OH)1606 (vs.) ν(N=CO–), 941 (s), 891 (s), ν(V=O). ^{1}H NMR (400 MHz, DMSO-d_6, Me_4Si): d (ppm): 8.83 (s, H, H–C=N), 7.73–6.71 (m, 10H, Ar–H). Electronic spectrum (λ_{max}, nm): 304, 330, 398.

2.4 General procedure for oxidative bromination

2.4.1 Procedure for method A: 1-(2-hydroxyphenyl)ethan-1-one (1a)

In a 50 mL round bottom flask equipped with a reflux condenser, vanadium(V) complex (5 mmol, 0.018 g), 1-(2-hydroxyphenyl)ethan-1-one (5 mmol, 0.68 g), and Bu_4NBr (2 mmol, 0.274 g) were placed. To the mixture, 5 mL of acetonitrile and trifluoroacetic acid (0.23 g, 2 mmol) were added. The flask was filled with oxygen (1 atm). The mixture was stirred at 70 °C for 4 h. The reaction mixture was then cool to room temperature and followed by treatment with aqueous sodium bicarbonate and extracted with ether. The organic layer was dried over Na_2SO_4, filtered, and evaporated. The product was purified by preparative column chromatography (TLC) (hexane/ethyl acetate = 2/1) solvents mixture to give 2-hydroxybenzoyl bromide in 96% yield.

2.4.2 Procedure for method B: 1-(2-hydroxyphenyl)ethan-1-one (1a)

In a 50 mL round bottom flask equipped with a reflux condenser, vanadium(V) complex (5 mmol, 0.018 g), 1-(2-hydroxyphenyl)ethan-1-one (5 mmol, 0.68 g), and Bu_4NBr (2 mmol, 0.274 g) were placed. To the mixture, 5 mL of acetonitrile and $AlCl_3$ (0.26 g, 2 mmol) were added. The flask was filled with oxygen (1 atm). The mixture was stirred at 70 °C for 4 h. The reaction mixture was then cool to room temperature and followed by addition of aqueous sodium bicarbonate and extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and evaporated. The product was purified by preparative column chromatography (TLC) (hexane/ethyl acetate = 2/1) solvents mixture to give 2-hydroxybenzoyl bromide in 96% yield.

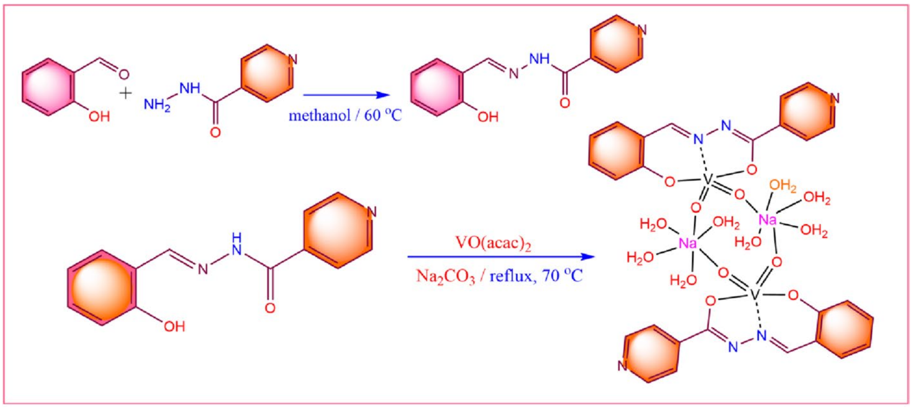
2.5 Gram-scale reaction of 2-hydroxybenzaldehyde

In a 100 mL two neck round bottom flask, vanadium(v) complex (0.1 g, 10 mmol), $AlCl_3$ (1.03 g, 10 mmol) was added. The flask was evacuated and backfilled with oxygen (1 atm), and 50 mL of acetonitrile and 2.44 g of 2-hydroxybenzaldehyde (20 mmol) were added. The reaction mixture was stirred at 70 °C for 4 h, cool to room temperature and extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and evaporated. Column chromatography gave 2.38 g of 5-bromo-2-hydroxybenzaldehyde with 97% yield.

3 Results and discussion

3.1 Synthesis and characterization

Vanadium(V) complex was obtained by reaction of vanadium pentoxide with ligand and sodium carbonate in 1:1:1 molar ratio (Scheme 3). Different spectroscopic techniques such Infrared spectroscopy, UV-visible spectroscopy and ^{1}H NMR were used to characterized the complex. In the IR spectrum of the complex, the peaks appeared at 3485 cm^{-1}, 1606 cm^{-1}, 941 cm^{-1} and 891 cm^{-1}, respectively. The peak at 3485 cm^{-1} was assigned to the –OH stretching vibrations frequency, whereas the peak at 1606 cm^{-1} was assigned to azomethine functional group (N=C) stretching vibrations frequency. The new stretching vibrations frequencies appeared at 941 cm^{-1} and 891 cm^{-1} in the IR spectrum of the complex, these peaks were assigned to the terminal V=O stretching vibrational frequencies. The ^{1}H NMR spectral data of the complex were recorded using DMSO-*d*$_6$ solution and the data were presented in the experimental section. The



Scheme 3 Schematic diagram showing the preparation of ligand (H_2SL) and complex (VO_2SL)

azomethine proton appeared at 8.83 ppm and the peaks in the region 7.73–6.71 ppm were assigned to the aromatic protons. The electronic spectrum of the complex shows two bands at 304 nm and 330 nm. The bands at 304 nm was assigned to intra-ligand transition whereas the bands at 398 nm was assigned to the ligand to metal charge transfer (LMCT) which arises from the transfer of charge from p-orbital of phenolate-oxygen atoms to an empty d-orbital of vanadium(V) atom [29, 30].

3.2 Single crystal structure analysis

Single crystal of the complex suitable for single XRD analysis was obtained by slow evaporation of solvent mixture (DMF/H_2O) at room temperature after 1 week. The single crystal structure of vanadium(v) complex is shown in Fig. 1. The crystal structures data and structure refinement parameters are given in Table 1. The geometrical bond lengths and bond angles of the complex were presented in Tables S1 and S2. The complex crystallized in triclinic crystal system with P-1 space group, the asymmetric unit of the complex consist of one vanadium atom, two terminal oxygen atoms and ligand moiety, and one terminal oxido linked to sodium atom which is bonded to two water molecules. The asymmetric unit of the complex contains one additional crystallization water molecule. The ligand coordinated to vanadium(V) ion in tridentate fashion through –ONO– donors atoms. The penta-coordinated vanadium atom adopted a distorted square pyramidal geometry, in which the oxygen and nitrogen atoms occupied in the equatorial positions, whereas the two dioxo groups occupied in the apical position. The geometrical bond lengths around vanadium atom are 1.9021(15) Å (V1-O1); 1.9868(16) Å (V1-O2); 1.6163(16) Å (V1-O3); 1.6223(17) Å (V1-O4) and 2.1249(19) Å (V1-N1), whereas the bond lengths around sodium atom are 2.3904(19) Å (Na1-O4); 2.298(2) Å (Na1-O5); 2.374(2) Å (Na1-O6); 2.361(2) Å (Na1-O7), respectively. The meta–metal interactions bond distances in the complex are 3.5786(18) Å (Na1-Na1^1) and 3.2742(11) Å (V1-Na1^1), symmetry code (^{1}1-x, 2-y, 1-z).

The packing diagram is shown in Fig. 2. Crystal structure analysis shows the existence of hydrogen bonding, pi-pi stacking and other short molecular interactions such as O–H.O, O–H.N and C–H.O. The O–H.O interaction bond distances are 2.877(3) Å (O(8)–H(8B).O(1); 2.888(3) Å (O(7)–H(7B).O(3); 2.810(3) Å (O(7)–H(7 A).O(8); 2.974(2) Å (O(6)–H(6B).O(2); 2.793(3) Å (O(6)–H(6 A).O(8); 3.014(3) Å (O(5)–H(5 A).O(7).

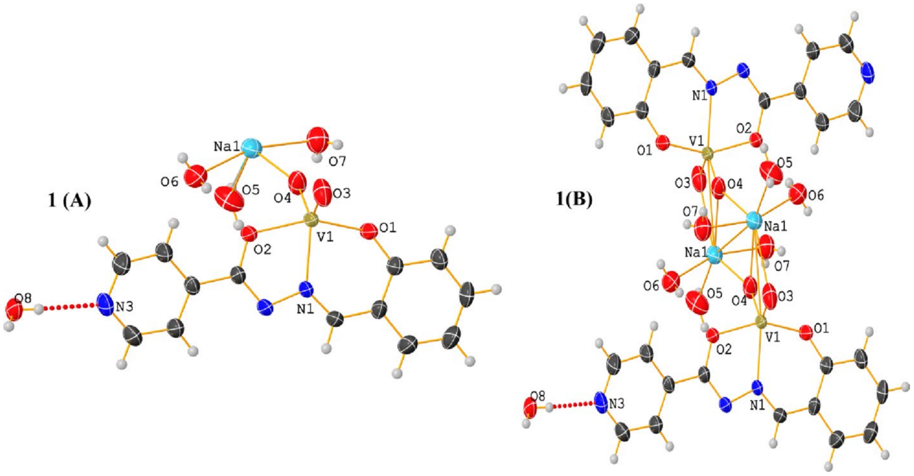


Fig. 1 Single crystal structure of vanadium(v) complex

Table 1 Crystal data and structure refinement

Empirical formula	$C_{26}H_{34}N_6Na_2O_{16}V_2$
Temperature/K	295.0(3)
Crystal system	Triclinic
Space group	P-1
a/Å	7.7307(5)
b/Å	10.3264(9)
c/Å	12.0317(9)
α/°	109.555(7)
β/°	104.336(6)
γ/°	93.128(6)
Volume/Å^3	866.91(12)
Z	2
ρ_{calc}g/cm^3	1.598
μ/mm^{-1}	0.645
F(000)	428.0
Radiation	MoKα (λ = 0.71073)
Reflections collected	4722
Independent reflections	3026 [R_{int} = 0.0204, R_{sigma} = 0.0416]
Data/restraints/parameters	3026/0/267
Goodness-of-fit on F^2	1.040
Final R indexes [I >= 2σ (I)]	R_1 = 0.0352, wR_2 = 0.0833
Final R indexes [all data]	R_1 = 0.0421, wR_2 = 0.0876
Largest diff. peak/hole/e Å^{-3}	0.33/− 0.26

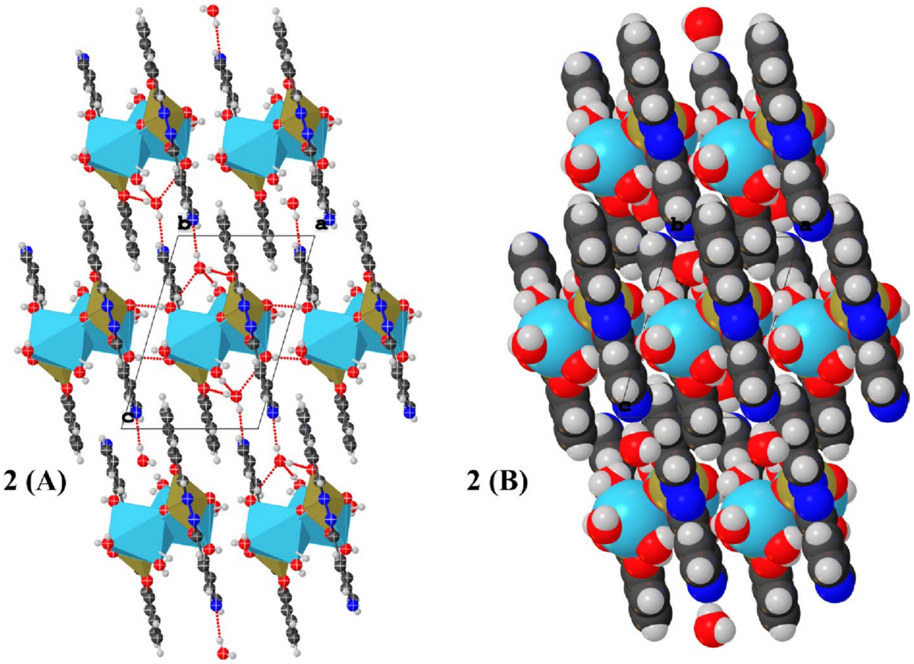


Fig. 2 **A** Packing diagram of the complex along the crystallographic b-axis and polyhedral plot for metal ions; **B** packing diagram of the complex along the b-axis showing a parallel stacking

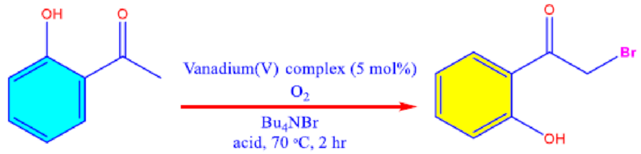
The O–H.N bond distances are 2.987(3) Å (O(5)–H(5B).N(2) and 2.803(3) Å O(8)–H(8 A).N(3), whereas the C–H.O interaction bond distances are 3.429(3) Å (C(4)–H(4).O(3) and 3.418(3) Å (C(7)–H(7).O(6), respectively. The major contribution are the

H···H interactions with 39%, followed by O···H interactions with 26.7%. The pi-pi stacking interaction bond distance between the centroid in the complex is 3.75 Å.

3.3 Oxidative bromination reaction

Using the above synthesized vanadium(V) complex, we carried out the experiment for oxidative bromination of organic substrates such as phenol, aniline, aromatic aldehyde and ketone. In the present work, we carried out the catalytic activities of vanadium(v) complex for the oxidative bromination of 1-(2-hydroxyphenyl)ethan-1-one using Bu_4NBr (as a bromide source) and Brønsted acid or Lewis acid in presence of oxygen (1 atm). In the initial stage, the oxidative bromination reaction of 1-(2-hydroxyphenyl) ethan-1-one using vanadium(v) complex (5 mol%), Bu_4NBr (300 mol%), trifluoroacetic acid (TFA) (300 mol%) using dioxane as a solvent and O_2 (1 atm) was carried out (Table 2). The bromination reaction proceeds smoothly leading to the formation of brominated product, 2-hydroxybenzoyl bromide with 96% yields within 2 h (Table 2, entry 1). In this study, we also performed the reaction under inert conditions using argon, but it was found that the bromination reaction yield only 14% (Table 2, entry 2). The use of p-toluenesulfonic acid monohydrate (PTS.H_2O) in place of trifluoroacetic acid (TFA) under identical conditions showed a 20% drop in yield (Table 2, entry 3). These results suggested that for effective catalytic bromination requires the use of acid and oxygen

Table 2 Optimization of reaction conditions for the oxidative bromination of 1-(2-hydroxyphenyl) ethan-1-one using vanadium(v) complex, Bu_4NBr and Brønsted acid or Lewis acid in presence of oxygen (1 atm)[a]



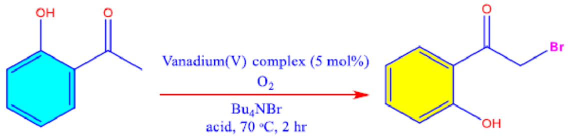
Entry	Vanadium (V) complex (mol%)	Bu_4NBr (mol%)	Acid/(mmol)	Isolated yield %
1[b]	5	300	CF_3COOH/300	87
2[b, d]	5	300	CF_3COOH/300	14
3	5	300	PTS. H_2O[c]/300	56
4	5	300	$AlCl_3$/300	39
5	5	150	$AlCl_3$/150	95
6	5	150	$BF_3.OEt_2$/150	45
7	5	150	$FeCl_3$/150	0
8	5	150	$ZnCl_2$/150	28
9	5	150	$CoCl_2$/150	0
10	5	150	$CuCl_2$/150	60
11	5	100	$AlCl_3$/100	57
12	5	50	$AlCl_3$/50	26
13	10	150	$AlCl_3$/150	74
14	2.5	150	$AlCl_3$/150	61
15	V_2O_5 (5 mol%)	150	$AlCl_3$/150	78
16	**No catalyst**	**150**	**$AlCl_3$/150**	**0**

[a] Conditions: 1-(2-hydroxyphenyl)ethan-1-one (5 mmol), 5 mol % vanadium(V) complex, Bu_4NBr (as bromide source), and acid, 5 mL of 1,4-dioxane, under O_2 (1 atm); [b] Conditions: 1-(2-hydroxyphenyl)ethan-1-one (3 mmol), 5 mol % vanadium(V) complex, Bu_4NBr (as bromide source), and acid, 5 mL of acetonitrile, under O_2 (1 atm); [c] p-Toluenesulfonic acid monohydrate; [d] Reaction under argon

(1 atm). The more important bromination reaction is thought to be accomplished by combining with a Lewis acid rather than a Brønsted acid. It should be mentioned that the 1-(2-hydroxyphenyl)ethan-1-one bromination process generated the 2-hydroxybenzoyl bromide in a reasonable yield (Table 2, entry 4). The amounts of $AlCl_3$ and the bromide source were successfully reduced to 120 mol% at 70 °C, in which the 2-hydroxybenzoyl bromide was produced in 95% isolated yield (Table 2, entry 5). The bromination reaction of 1-(2-hydroxyphenyl)ethan-1-one was also performed by using different amount of vanadium(v) complex (2.5 mol% and 10 mol%), Bu_4NBr (50 mol% and 150 mol%), $AlCl_3$ (50/100/150 mol%) but it was observed that the bromination products were obtained in less yield (Table 2, entries 11–14). The bromination reaction was also carried out using $BF_3.OEt_2$, $ZnCl_2$ and $CuCl_2$ instead of $AlCl_3$, but the bromination products were obtained in lower yield (Table 2, entries 6, 8 and 10). Other Lewis acid such as $FeCl_3$, and $CoCl_2$ are less effective for the oxidative generation of bromine from bromide salts under mild conditions compare to vanadium catalyst (Table 2, entries 7, 9). The catalytic study was also performed using V_2O_5, however the yield of 2-hydroxybenzoyl bromide obtained is lower compared to that of the complex (Table 2, entry 15). Furthermore, the catalytic study was also carried out without the use of the vanadium complex in order to check that there is no background with the conditions of Bronsted acids and Lewis acids (Table 2, entry 16).

The bromination reaction of 1-(2-hydroxyphenyl)ethan-1-one was also performed using different solvents combination such as acetonitrile, toluene, dichloromethane and 1,4-dioxane (Table 2). Hence, the bromination reaction in these solvents resulted in a slightly lower yield compared with acetonitrile as a solvent (Table 3, entries 1–6). Similarly, after studying the effects of solvents, the catalytic studies was also carried out using $AlCl_3$ as a Lewis acid under same condition and it is found that Lewis acid is much more superior compare to the trifluoroacetic acid system. The bromination reaction using toluene and acetonitrile as a solvent were also carried out at room temperature, it was found that reaction proceeded smoothly giving a moderate yield (Table 3, entries 7 and

Table 3 The effect of solvent in bromination of 1-(2-hydroxyphenyl)ethan-1-one using vanadium(V) complex, Bu_4NBr, Brønsted acid or Lewis acid in presence of oxygen (1 atm)[a]



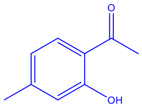
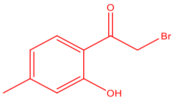
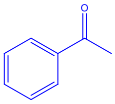
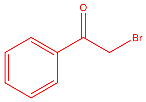
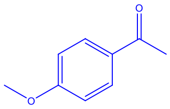
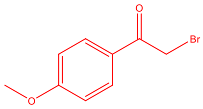
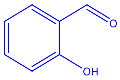
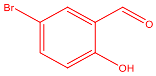
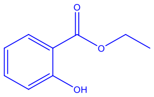
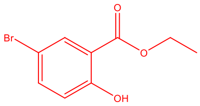
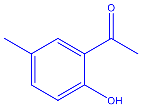
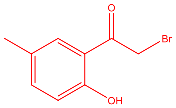
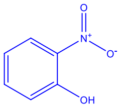
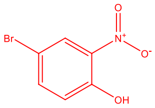
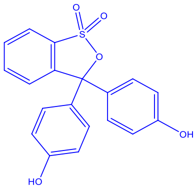
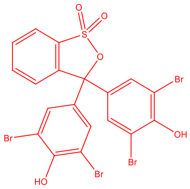
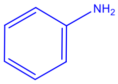
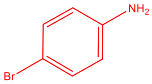
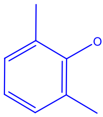
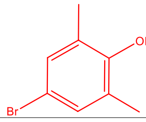
Entry	Vanadium(V) complex (mol%)	Bu_4NBr (mol%)	Acid/(mmol)	Solvent	Isolated yield %
1[b]	5	300	CF_3COOH/300	1,4-dioxane	62
2[b]	5	300	CF_3COOH/300	Toluene	67
3	5	300	CF_3COOH/300	Dichloromethane	38
4	5	150	$AlCl_3$/150	Acetonitrile	79
5	5	150	$AlCl_3$/150	Toluene	87
6	5	150	$AlCl_3$/150	Dichloromethane	65
7[c]	5	150	$AlCl_3$/150	Toluene	69
8[c]	5	150	$AlCl_3$/150	Acetonitrile	57

[a]Conditions: 1-(2-hydroxyphenyl)ethan-1-one (5 mmol), 5 mol % vanadium(v) complex, Bu_4NBr (as bromide source) and acid, 5 mL of acetonitrile, under O_2 (1 atm); [b]Conditions: 1-(2-hydroxyphenyl)ethan-1-one (3 mmol), 5 mol % vanadium(v) complex, Bu_4NBr (as bromide source), and acid, 5 mL of acetonitrile, under O_2 (1 atm). [c]Reaction was conducted at room temperature (23 °C)

8). The reversal of performance between room temperature and at elevated temperature can be explained by considering the nature of the solvents. At room temperature it can be attributed that acetonitrile coordinates with $AlCl_3$, and partially deactivated the catalyst by occupying its vacant orbital. However, as the temperature increases the coordination shifted and liberating more active $AlCl_3$ to facilitate the generation of the Br^+ electrophile. Similarly, in case of toluene, which is a non-polar and a weakly coordinating solvent which allows for maximum catalytic efficiency. Furthermore, the performance between Lewis Acid and Brønsted acid relies on the formation of $Br^+AlCl_4^-$ complex. Solvents with strong coordinating abilities like acetonitrile may compete directly with the halogen for the Aluminium center. In Trifluoroacetic acid (TFA) the solvents effects are governed by acidity and ability to stabilize protons (H^+) rather than electron-pair coordination [31].

To investigate the substrate scope and explore the validity of the present catalytic system, we explore the catalytic oxidative bromination reaction using different substrates. The reaction was performed using the standardised method, vanadium(v) complex (as a catalyst), Bu_4NBr (as a bromide source), trifluoroacetic acid, $AlCl_3$ (Lewis acid) in presence of O_2 (1 atm) and acetonitrile as a solvent at 70 °C for 4 h as shown in Table 4. The oxidative bromination of 1-(2-hydroxy-4-methylphenyl)ethan-1-one **(1)** proceeded smoothly giving 2-bromo-1-(2-hydroxy-4-methylphenyl)ethan-1-one (Table 4, entry 1). It was observed that the use of trifluoroacetic acid, the yield of 2-bromo-1-(2-hydroxy-4-methylphenyl)ethan-1-one dropped to 18%. Similarly the bromination reaction of acetophenone **(2)** gives 2-bromo-1-phenylethan-1-one in high yield in the presence of 120 mol % of $AlCl_3$ and Bu_4NBr (Table 4, entry 2). Bromination reaction of 1-(4-methoxyphenyl)ethan-1-one **(3)** and 2-hydroxybenzaldehyde **(4)** was successfully converted to 2-bromo-1-(4-methoxyphenyl)ethan-1-one with 91% and 5-bromo-2-hydroxybenzaldehyde 98% (Table 4, entries 3 and 4). The use of trifluoroacetic acid instead of $AlCl_3$ drop the yield of 2-bromo-1-(4-methoxyphenyl)ethan-1-one to 21% and 5-bromo-2-hydroxybenzaldehyde to 17%. The efficiency of $AlCl_3$ than trifluoroacetic acid was also observed in the oxidative bromination reaction. Ethyl 2-hydroxybenzoate **(5)** and 1-(2-hydroxy-5-methylphenyl)ethan-1-one **(6)** was converted to their corresponding bromide **6a** and **7a** with 90% and 94% yield, respectively (Table 4, entries 5 and 6). Similarly, the bromination reaction of 2-nitrophenol **(7)**, aniline **(8)**, phenol red **(9)** and 2,6-dimethylphenol (**10**) was performed smoothly and converted to their corresponding bromide **8a** (91%) and **9a** (96%), **10a** (86%) and **11a** (94%), respectively (Table 4, entries 7–10). It has been observed that the position of attack for bromination reactions are governed by the electron donating and electron withdrawing attached to the ring. Strong electron withdrawing group present on the ring such as –CHO and NO_2 lack alpha hydrogen and deactivate the ring and the bromination reaction takes place at the meta-position because it is the least destabilized site for the carbocation intermediate. Substituents that are electron donation group increase the electron density at the ortho and para position, and hence the bromination reaction take place at the orth-position or the para-position. However, aromatic ketones having acidic alpha hydrogen can undergoes keto-enol tautomerism, and the bromination take place at the alpha position rather than on the aromatic ring because the enol form acts as a strong nucleophile. The results obtained from the catalytic studies show that vanadium(v) complex is a good catalyst for oxidative bromination reaction using Brønsted acid or Lewis acid in presence of oxygen

Table 4 Oxidative bromination using vanadium(V) complex/$Bu_4NBr/AlCl_3$/ in presence of oxygen (1 atm)[a]

Entry	Substrate	Condition [a, b]	Product	Yield (%) (isolated)
1		A, 150 B, 300		2a, 98 2a, 80
2		A, 150 B, 300		3a, 92 3a, 79
3		A, 150 B, 300		4a, 91 4a, 70
4		A, 150 B, 300		5a, 98 5a, 81
5		A, 150 B, 300		6a, 90 6a, 78
6		A, 150 B, 300		7a, 94 7a, 78
7		A, 150 B, 300		8a, 91 8a, 71
8		A, 150 B, 300		9a, 96 9a, 70
9		A, 150 B, 300		10a, 86 10a, 76
10		A, 150 B, 300		11a, 96 11a, 80

[a]Method: Amount of Bu_4NBr and $AlCl_3$ (mol %); [b]Method A: 5 mmol of substrate, 5 mol % vanadium(V) complex, Bu_4NBr, $AlCl_3$, 5 mL of acetonitrile, under O_2 (1 atm), 70 °C, 4 h. Method B: 5 mmol of substrate, 5 mol % vanadium(V) complex, Bu_4NBr, Trifluoroacetic acid, 5 mL of acetonitrile, under O_2 (1 atm), 70 °C, 4 h

(1 atm) and Bu_4NBr as a bromide source. Based on the aforementioned findings, it is anticipated that $AlBr_3$ will function as both a source of bromide ions and a Lewis acid. The bromination of acetophenone was carried out with 5 mol % of vanadium(v) complex and 120 mol % of $AlBr_3$ under oxygen (1 atm). It was found that the bromination reaction proceeded successfully which lead to the formation of the 2-bromo-1-phenylethan-1-one with 87% yield. In oxidative bromination systems, $AlBr_3$ provides the Br^- ions for the reaction. These ions are oxidized to electrophilic species (Br_2 or Br^+) forming more reactive electrophilic intermediate such as bromonium ions facilitating the electrophilic substitution. Studies have shown that $AlBr_3$ can acts as a direct brominating agent, converting the organic substrates into brominated derivatives without the initial addition

of elemental Br_2. In bromination reactions, $AlBr_3$ outperforms $AlCl_3$ and TFA due to its stronger Lewis acidity and its role as a halogen donor [23]. This result indicates that two bromides of $AlBr_3$ are able to participate as a bromide source.

Notably, a gram-scale practical reaction was carried out successfully to give the bromination product in a high yield, as exemplified by the bromination of 2-hydroxybenzaldehyde to the corresponding 5-bromo-2-hydroxybenzaldehyde in 97% isolated yield.

Furthermore, the catalyst can be recycled, regenerate and used for further reaction. Hence, we have successfully executed the bromination experiment of 2-hydroxyacetophenone for five consecutive runs, in order to study the feasibility of the catalyst (Fig. 3). In our studies, the catalyst can be easily recovered, using a simple extraction method, washed with ethylacetate and dried at 80 °C for 40 min. In the following cycles, the recovered catalyst was kept for further use. These findings demonstrated that neither deactivation nor decrease the catalyst's selectivity occurred during the cycles.

4 Plausible mechanisms

It has been known that the bromide ions are oxidized by the stoichiometric oxo-metal [32]. While one electron transfer was observed with the chromium ion, manganese and ruthenium complexes has been also reported which induces the formation of hypobromide species through oxygen atom transfer [33, 34]. In the current study, the oxidative bromination of 2,6-demethylphenol did not produce benzyl bromide nor a dimerization product through radical process (Table 4, entry 10). Therefore, a bromonium species ($OBr/AlBr_2$, Br^+) may be suggested as the key intermediate. This species is produced by oxidation of a bromide ion via oxygen atom transfer of an oxovanadium species activated by a Lewis acid. Hence, the catalytic efficiency of the bimetallic complex is attributed to a cooperative effect between the two metal centres as shown in the proposed mechanism (Scheme 4). The catalytic cycle initiates with the formation of vanadium peroxo intermediate upon reaction with the oxidant. In the next step, the Al(III) center functions as a Lewis acid, coordinating to the peroxo-oxygen atom. This secondary coordination

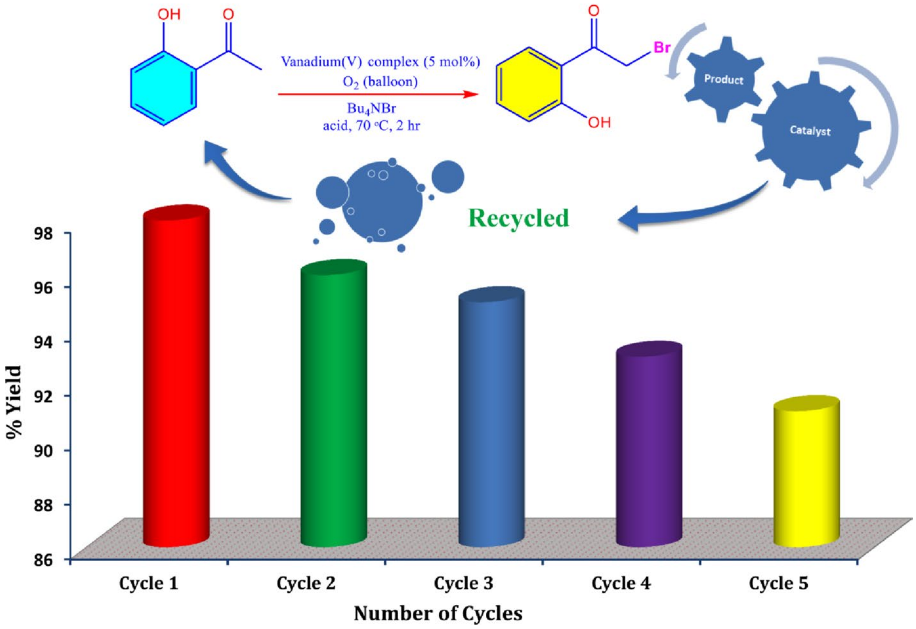
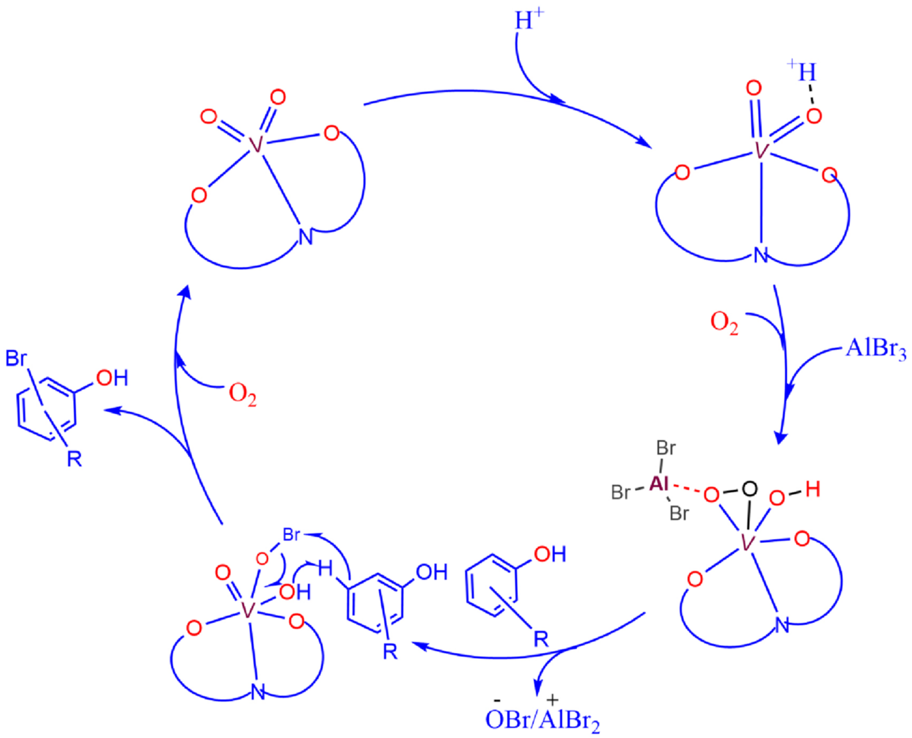


Fig. 3 Recyclability of the catalyst



Scheme 4 Plausible mechanism for the catalytic oxidative bromination

induces a strong polarization of the V-O bond, thereby significantly increasing the electrophilicity of the vanadium center and facilitates the nucleophilic attack of the substrates regeneration of the catalyst in presence of oxygen.

5 Conclusion

In conclusion, vanadium(v) complex was successfully synthesis and characterized. The complex adopted a square pyramidal geometry. The catalytic activity for bromination of various organic substrates was obtained in good yield without the use of a strong oxidant. Using aluminium halide as a Lewis acid instead of a Brønsted acid allows for more efficient and practical selective bromination of a variety of substrates. The oxidation of bromide anion proceeds to produce a species that id similar to a bromonium ion through the combination of a Lewis acid and a vanadium catalyst. It was found that $AlBr_3$ acted as a Lewis acid and a source of bromide, resulting in smooth bromination without the need for a protic acid or stoichiometric strong oxidant. Research is being done to increase the synthetic flexibility and employ this practical method for other reactions.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1007/s44371-026-00557-0.

Supplementary Material 1.

Acknowledgements
The author are thankful to thank Head SAIF, North-Eastern Hill University, Shillong, Meghalaya-793022, India for providing 1 H & 13 C NMR spectra, Head, Department of Chemistry, NEHU for single crystal XRD data.

Author contributions

Sunshine Dominic Kurbah: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Ndege Simisi Clovis: Writing – review & editing, Visualization, Investigation, Validation, Formal analysis, Data curation.

Funding

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

Data availability

Yes, all data generated or analysed during this study are included in this published article [and its supplementary files].

Declarations

Ethics approval and consent to participate

This research did not involve human participants or animal experiments, and therefore ethical approval was not required.

Consent for publication

All authors have reviewed the manuscript and consent to its publication.

Competing interests

The authors declare no competing interests.

Received: 31 October 2025 / Accepted: 20 February 2026

References

1. Horvath IT, Introduction: sustainable chemistry. Chem Rev. 2018;118:369–71. https://doi.org/10.1021/acs.chemrev.7b00721.
2. MacKellar JJ, Constable DJC, Kirchhoff MM, Hutchison JE, Beckman E. Toward a green and sustainable chemistry education road map. J Chem Educ. 2020;97:2104–13. https://doi.org/10.1021/acs.jchemed.0c00288.
3. Ganesh KN, Zhang D, Miller SJ, Rossen K, Chirik PJ, Kozlowski MC, Zimmerman JB, Brooks BW, Savage PE, Allen DT, Voutchkova-Kostal AM. Green chemistry: a framework for a sustainable future. Organometallics. 2021;40:1801–5. https://doi.org/10.1021/acs.organomet.1c00343.
4. Murcia JE, Martinez S, Martins V, Herrera D, Buitrago C, Velasquez A, Ruiz F, Torres M. Risk assessment and green chemistry applied to waste generated in university laboratories. Heliyon. 2023;9:e15900. https://doi.org/10.1016/j.heliyon.2023.e15900.
5. World Commission on Environment and Development Our Common Future. Oxford University Press: Oxford. 1987. http://www.un-documents.net/ocf-a2.htm
6. Debecker DP, Hii KK, Moores A, Rossi LM, Sels B, Allen DT, Subramaniam B. Shaping effective practices for incorporating sustainability assessment in manuscripts submitted to ACS sustainable chemistry & engineering: catalysis and catalytic processes. ACS Sustainable Chem Eng. 2021;9:4936–40. https://doi.org/10.1021/acssuschemeng.1c02070.
7. Idul JJA, Walag AMP. Integrating green chemistry and sustainability principles to a secondary science curriculum: a mixed-methods needs assessment. J Chem Educ. 2024;101:2765–78. https://doi.org/10.1021/acs.jchemed.4c00341.
8. Centi G, Perathoner S. Catalysis and sustainable (green) chemistry. Catal Today. 2003;77:287–97. https://doi.org/10.1016/S0920-5861(02)00374-7.
9. Centi G, Perathoner S. Catalysis and sustainable (green) chemistry. Catal Today. 2000;55:11–22. https://doi.org/10.1016/S0920-5861(99)00222-9.
10. Day EL, Petritis SJ, McFall-Boegeman H, Starkie J, Zhang M, Cooper MM. A framework for the integration of green and sustainable chemistry into the undergraduate curriculum: greening our practice with scientific and engineering practices. J Chem Educ. 2024;101:1847–57. https://doi.org/10.1021/acs.jchemed.3c00737.
11. Cannon AS, Warner JC, Vidal JL, O'Neil NJ, Nyansa MMS, Obhi NK, Moir JW. A promise to a sustainable future: 10 years of the green chemistry commitment at beyond benign. Green Chem. 2024;26:6983–93. https://doi.org/10.1039/D4GC00575A.
12. Freese T, Elzinga N, Heinemann M, Lerch MM, Feringa BL. The relevance of sustainable laboratory practices. RSC Sustain. 2024;2:1300–36. https://doi.org/10.1039/D4SU00056K.
13. Byrne FP, Jin S, Paggiola G, Petchey THM, Clark JH, Farmer TJ, Hunt AJ, McElroy CR, Sherwood J. Tools and techniques for solvent selection: green solvent selection guides. Sustainable Chem Processes. 2016;4:7. https://doi.org/10.1186/s40508-016-0051-z.
14. Anastas PT, Warner JC. Green chemistry: theory and practice. Oxford: OxfordUniversity; 1998. https://doi.org/10.1093/oso/9780198506980.001.0001.
15. Anastas PT, Kirchhoff MM, Williamson TC. Catalysis as a foundational pillar of green chemistry. Appl Catal A. 2001;221:3–13. https://doi.org/10.1016/S0926-860X(01)00793-1.
16. Gladysz JA. Recoverable catalysts. Ultimate goals, criteria of evaluation, and the green chemistry interface. Pure Appl Chem. 2001;73:1319–24. https://doi.org/10.1351/pac200173081319.
17. Molnar A, Papp A. Catalyst recycling-a survey of recent progress and current status. Coord Chem Rev. 2017;349:1–65. https://doi.org/10.1016/j.ccr.2017.08.011.
18. Hayler JD, Leahy DK, Simmons EM. A pharmaceutical industry perspective on sustainable metal catalysis. Organometallics. 2019;38:36–46. https://doi.org/10.1021/acs.organomet.8b00566.
19. Langeslay RR, Kaphan DM, Marshall CL, Stair PC, Sattelberger AP, Delferro M. Catalytic applications of vanadium: a mechanistic perspective. Chem Rev. 2019;119:2128–91. https://doi.org/10.1021/acs.chemrev.8b00245.

20. Holzwarth MS, Plietker B. Biorelevant metals in sustainable metal catalysis-a survey. ChemCatChem. 2013;5:1650–79. https://doi.org/10.1002/cctc.201200592.
21. Pessoa JC, Maurya MR. Vanadium complexes supported on organic polymers as sustainable systems for catalytic oxidations. Inorg Chim Acta. 2017;455:415–28. https://doi.org/10.1016/j.ica.2016.04.012.
22. Scott WW, Layfield EB. Characteristics of a vanadium catalyst and a new catalyst for sulfuric acid. Ind Eng Chem. 1931;23:617–20. https://doi.org/10.1021/ie50258a004.
23. Kikushima K, Moriuchi T, Hirao T. Vanadium-catalyzed oxidative bromination promoted by Brønsted acid or Lewis acid. Tetrahedron. 2010;66:6906–11. https://doi.org/10.1016/j.tet.2010.06.042.
24. Rothenberg G, Clark JH. Vanadium-catalysed oxidative bromination using dilute mineral acids and hydrogen peroxide: an option for recycling waste acid streams. Org Proc Res Dev. 2000;4:270–4. https://doi.org/10.1021/op000020l.
25. Kurbah SD, Lal RA. Bioinspired catalysis and bromoperoxidase like activity of a multistimuli-responsive supramolecular metallogel: supramolecular assembly triggered by pi-pi stacking and hydrogen bonding interactions. New J Chem. 2020;44:5410–8. https://doi.org/10.1039/c9nj05732c.
26. Kurbah SD. One pot synthesis of oximes from carbonyl compounds catalysed by vanadium(V) complex. Curr Catal. 2022;11:127–33. https://doi.org/10.2174/2211544712666230103163911.
27. Sheldrick GM. A short history of SHELX. Acta Cryst. 2008;A64:112–22. https://doi.org/10.1107/S0108767307043930.
28. Sheldrick GM. Crystal structure refinement with SHELXL. Acta Crystallogr C Struct Chem Commun. 2015;71:3–8. https://doi.org/10.1107/S2053229614024218.
29. Samanta S, Ghosh D, Mukhopadhyay S, Endo A, Weakley TJR, Chaudhury M. Oxovanadium(IV) and (V) complexes of dithiocarbazate-based tridentate schiff base ligands: syntheses, structure, and photochemical reactivity of compounds involving imidazole derivatives as coligands. Inorg Chem. 2003;42:1508. https://doi.org/10.1021/ic020438v.
30. Maurya MR, Nandi M, Kumar S, Gupta P, Avecilla F. Symmetrical bis-hydrazone ligand-based binuclear oxido/dioxido-vanadium(IV/V) complexes: synthesis, reactivity, and catalytic applications for the synthesis of biologically potent 2-phenylquinazolin-4-(3H)-ones. Inorg Chem. 2025;64:1734. https://doi.org/10.1021/acs.inorgchem.4c04035.
31. Abraham MH, Grellier PL, Abboud JLM, Doherty RM, Taft RW. Solvent effects in organic chemistry-recent developments. Can J Chem. 1988;66(11):2673–86. https://doi.org/10.1139/v88-420.
32. Jin N, Bourassa JL, Tizio SC, Groves JT. Rapid, reversible oxygen atom transfer between an oxomanganese(v) porphyrin and bromide: a haloperoxidase mimic with enzymatic rates. Angew Chem Int Ed. 2000;39:3849–51. https://doi.org/10.1002/1521-3773(20001103)39. :21%3C3849::AID-ANIE3849%3E3.0.CO;2-0.
33. Lam WWY, Man WL, Wang YN, Lau TC. Kinetics and mechanisms of the oxidation of iodide and bromide in aqueous solutions by a trans-dioxoruthenium(VI) complex. Inorg Chem. 2008;47:6771–8. https://doi.org/10.1021/ic8003849.
34. Hung M, Bakac A. Kinetics and mechanism of acid-catalyzed oxidation of bromide ions by the aqueous chromyl(IV) ion. Inorg Chem. 2005;44(25):9293–8. https://doi.org/10.1021/ic051310r.

Publisher's note