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Impact of ambient gases on the mechanism of [Cs$_8$Nb$_6$O$_{19}$]-promoted nerve-agent decomposition†‡

Alexey L. Kaledin, Darren M. Driscoll, Diego Troya, Daniel L. Collins-Wildman, Craig L. Hill, John R. Morris and Djamaladdin G. Musaev

The impact of ambient gas molecules (X), NO$_2$, CO$_2$ and SO$_2$ on the structure, stability and decontamination activity of Cs$_8$Nb$_6$O$_{19}$ polyoxometalate was studied computationally and experimentally. It was found that Cs$_8$Nb$_6$O$_{19}$ absorbs these molecules more strongly than it adsorbs water and Sarin (GB) and that these interactions hinder nerve agent decontamination. The impacts of diamagnetic CO$_2$ and SO$_2$ molecules on polyoxoniobate Cs$_8$Nb$_6$O$_{19}$ were fundamentally different from that of NO$_2$ radical. At ambient temperatures, weak coordination of the first NO$_2$ radical to Cs$_8$Nb$_6$O$_{19}$ conferred partial radical character on the polyoxoniobate and promoted stronger coordination of the second NO$_2$ adsorbent to form a stable diamagnetic Cs$_8$Nb$_6$O$_{19}$/(NO$_2$)$_2$ species. Moreover, at low temperatures, NO$_2$ radicals formed stable dinitrogen tetraoxide (N$_2$O$_4$) that weakly interacted with Cs$_8$Nb$_6$O$_{19}$. It was found that both in the absence and presence of ambient gas molecules, GB decontamination by the Cs$_8$Nb$_6$O$_{19}$ species proceeds via general base hydrolysis involving: (a) the adsorption of water and the nerve agent on Cs$_8$Nb$_6$O$_{19}$(X), (b) concerted hydrolysis of a water molecule on a basic oxygen atom of the polyoxoniobate and nucleophilic addition of the nascent OH group to the phosphorus center of Sarin, and (c) rapid reorganization of the formed pentacoordinated-phosphorus intermediate, followed by dissociation of either HF or isopropanol and formation of POM-bound isopropyl methyl phosphonic acid (i-MPA) or methyl phosphonofluoridic acid (MPFA), respectively. The presence of the ambient gas molecules increases the energy of the intermediate stationary points relative to the asymptote of the reactants and slightly increases the hydrolysis barrier. These changes closely correlate with the Cs$_8$Nb$_6$O$_{19}$−X complexation energy. The most energetically stable intermediates of the GB hydrolysis and decontamination reaction were found to be Cs$_8$Nb$_6$O$_{19}$/X-MPFA−(i-PFOH) and Cs$_8$Nb$_6$O$_{19}$/X−(i-MPA)−HF both in the absence and presence of ambient gas molecules. The high stability of these intermediates is due to, in part, the strong hydrogen bonding between the adsorbates and the protonated [Cs$_8$Nb$_6$O$_{19}$/X]$^+$-core. Desorption of HF or and (i-PFOH) and regeneration of the catalyst required deprotonation of the [Cs$_8$Nb$_6$O$_{19}$/X]$^+$-core and protonation of the phosphonic acids i-MPA and MPFA. This catalyst regeneration is shown to be a highly endothermic process, which is the rate-limiting step of the GB hydrolysis and decontamination reaction both in the absence and presence of ambient gas molecules.

Introduction

The design of materials that can rapidly, fully, and catalytically decontaminate chemical warfare agents (CWAs) and other toxic compounds is an increasingly active area of research and one that presents some questions in fundamental chemistry.$^{1-3}$ As suggested by enzymatic chemistry, some of the most effective strategies for CWA destruction involve catalyzed hydrolysis reactions.$^4$ Specifically, it is well established that the P−X bonds (X = F, CN, SR, etc.) of organophosphorus (OP) nerve agents rapidly inactivate acetylcholinesterase (a serine hydrolase), the enzyme that facilitates hydrolysis of the neurotransmitter acetylcholine in the nervous system. This inactivation occurs through rapid nucleophilic addition and irreversible binding of
the serine OH to the phosphorus atom of the nerve agent. Thus, an atomistic/molecular level understanding of the hydrolysis of OP compounds by nucleophilic addition and other processes may lead to the development of more effective materials and catalysts for nerve agent decontamination. Ongoing research efforts have identified several organic and inorganic materials, including metal–organic frameworks (MOFs, especially UiO-66, NU-1000 and MOF-808),10–18 polyoxometalates (POMs),11–14 MOF/POM hybrid materials,15,16 zirconium hydroxide,17 zeolites,18 and organic polymers,19 as effective OP hydrolysis materials.

Recently, the use of POMs to catalyze nerve agent decontamination has attracted wide attention, in part because POMs are molecular representations of metal oxides and are thus far more amenable than the latter to extensive synthetic compositional alteration and characterization at the molecular level.20,21 Polyoxoniobates (PONbs), including [Nb6O19]8−, are effective OP nerve agent hydrolysis compounds because their high negative charge densities (negative charge per polyanion oxygen) render them highly basic and nucleophilic. Thus, it is not surprising that the synthesis and in-depth analysis of the structures and reactivities of various (alkali and organic) salts of PONbs continue to be the focus of extensive studies.22,23 These studies show that the structures and, consequently, the catalytic activities of these materials for nerve agent decontamination depend on many factors, including (but not limited to) the nature of the counter-cation, the pH of the solution, the aggregate state (powder or solid-state material) of the catalyst, the real-time environmental conditions, and the nature and concentration of ambient gas molecules.

Earlier research on Lindqvist hexaniobiate alkali salts (M2Nb6O19, M = Li, K, Cs) reported rapid hydrolysis of the OP agent Sarin (GB, propan-2-yl methylphosphonofluoridate, see Scheme 1) both in aqueous solution and at the gas–surface interface.11 Small-angle X-ray scattering (SAXS) measurements showed aggregation of the OP compounds on the polyoxoniobate (PONb), which led to the suggestion that the reaction follows a general base hydrolysis mechanism.12 Our subsequent computational study on the mechanism of decomposition of GB by a Cs-salt of PONb, Cs8Nb6O19 (or CsPONb), confirmed the general base hydrolysis mechanism of this reaction at the gas–surface interface.24

Briefly, we have found that GB degradation by Cs8Nb6O19 includes the following elementary steps (see Scheme 1): (a) the adsorption of water and the nerve agent on the Cs8Nb6O19 species, (b) concerted dissociation of the adsorbed water molecule on a basic oxygen atom of the polyoxoniobate and nucleophilic addition of the nascent OH group to the phosphorus center of the nerve agent, (c) rapid reorganization of the resulting pentacoordinated phosphorus intermediate by dissociation of either HF or isopropanol, and formation of POM-bound isopropyl methyl phosphonic acid (i-MPA) or methyl phosphonoﬂuoridic acid (MPFA), respectively. The calculations showed that the phosphonic acids i-MPA and MPFA are strongly bound to the protonated [Cs8Nb6O19H]core through hydrogen bonds and electrostatic interactions with the Cs counter-ions, suggesting that full catalyst regeneration may require additional treatment and depends on the nature of the counterions as well as the real-time (ambient) experimental conditions.

Although PONb catalysts have been shown to react with CWAs, the chemistry has yet to be characterized in the presence of ambient gases (for example, NO2, CO2 and SO2), which may affect the stabilities, structural motifs, and activities of the PONb catalysts. Because this issue is vital to the application of PONbs as decontamination catalysts in real conditions, this paper probes the impact of the common battlefield contaminants NO2, CO2 and SO2 on the structure, stability and decontamination activity of the exemplary PONb species Cs8Nb6O19. This study addresses in depth the effects of these ambient gases on the structures of the catalysts and the base hydrolysis mechanism for Sarin degradation using density functional theory (DFT) calculations and infrared (IR) spectroscopy.

**Results and discussion**

**A. Structure of Cs8Nb6O19 in the presence of gaseous CO2, NO2 and SO2**

Here, we divide our discussion into two subsections. First, we discuss the interaction of diamagnetic CO2 and SO2 molecules with Cs8Nb6O19; then, we present our findings on the interactions between NO2 radical and Cs8Nb6O19.

**A1. Structure of Cs8Nb6O19 in the presence of gaseous CO2 and SO2.** Our calculations reveal that Cs8Nb6O19 very strongly binds the ambient gas molecules CO2 and SO2 at various (terminal O− and/or bridging O=) sites to form Cs8Nb6O19/X adducts. As reported in Table 1, where we present the calculated adsorption energies, there is a clear preference of adsorption of both CO2 and SO2 at the terminal oxygen site rather than at the bridging oxygen site. Indeed, the calculated enthalpies and free energies of adsorption (presented as ΔH/ΔG) of Cs8Nb6O19 + X → Cs8Nb6O19/X upon coordination of X to the O− and O= sites are −29.0/−23.2 and −16.7/−10.8 kcal mol−1 for X = CO2 and −47.6/−40.3 and −34.1/−26.6 kcal mol−1 for X = SO2, respectively.

The factors that impact the strength of the Cs8Nb6O19/X bonding and site-preference of adsorption were analyzed by investigating the resulting geometries of these complexes. From Fig. 1, where we present the most important geometries of the
Table 1  Adsorption energies (total electronic $E$, enthalpy $H$ and Gibbs free energy $G$ in kcal mol$^{-1}$) defined as energy differences of the complex Cs$_8$Nb$_6$O$_{19}$/X and its two separated fragments, Cs$_8$Nb$_6$O$_{19}$ + X, where X = CO$_2$, NO$_2$ and SO$_2$, as shown in the leftmost column. The superscripts “c” and “μ” indicate the position where the molecule is adsorbed on Cs$_8$Nb$_6$O$_{19}$. $\text{Cs}^2$ indicates NO$_2$ adsorption to two Cs counter-cations in a symmetric manner.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta E$</th>
<th>$\Delta H$</th>
<th>$\Delta G$</th>
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<td>$\text{O}^\text{c}$: Cs$_8$Nb$<em>6$O$</em>{19}$ + CO$_2$</td>
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<td>$\text{O}^\text{μ}$: Cs$_8$Nb$<em>6$O$</em>{19}$ + CO$_2$</td>
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<td>$-16.7$</td>
<td>$-10.8$</td>
</tr>
<tr>
<td>$\text{O}^\text{c}$: Cs$_8$Nb$<em>6$O$</em>{19}$ + SO$_2$</td>
<td>$-48.2$</td>
<td>$-47.6$</td>
<td>$-40.3$</td>
</tr>
<tr>
<td>$\text{O}^\text{μ}$: Cs$_8$Nb$<em>6$O$</em>{19}$ + SO$_2$</td>
<td>$-34.7$</td>
<td>$-34.1$</td>
<td>$-26.6$</td>
</tr>
<tr>
<td>Cs$_8^\text{C}^\text{2}$: Cs$_8$Nb$<em>6$O$</em>{19}$ + NO$_2$</td>
<td>$-21.7$</td>
<td>$-22.2$</td>
<td>$-22.1$</td>
</tr>
<tr>
<td>$\text{O}^\text{c}$: Cs$_8$Nb$<em>6$O$</em>{19}$ + NO$_2$</td>
<td>$-18.8$</td>
<td>$-18.7$</td>
<td>$-13.9$</td>
</tr>
<tr>
<td>Cs$_8^\text{C}^\text{3}$ and $\text{O}^\text{μ}$: Cs$_8$Nb$<em>6$O$</em>{19}$ + 2NO$_2$</td>
<td>$-77.4$</td>
<td>$-74.6$</td>
<td>$-58.0$</td>
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<tr>
<td>Cs$_8$Nb$<em>6$O$</em>{19}$/CO$_2$(O$^\text{μ}$) + H$_2$O</td>
<td>$-24.2$</td>
<td>$-22.4$</td>
<td>$-11.9$</td>
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<td>Cs$_8$Nb$<em>6$O$</em>{19}$/SO$_2$(O$^\text{μ}$) + H$_2$O</td>
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<td>$-17.3$</td>
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<tr>
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<td>$-17.4$</td>
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<tr>
<td>Cs$_8$Nb$<em>6$O$</em>{19}$/H$_2$O/CO$_2$(O$^\text{μ}$) + GB</td>
<td>$-18.0$</td>
<td>$-17.4$</td>
<td>$-2.4$</td>
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<tr>
<td>Cs$_8$Nb$<em>6$O$</em>{19}$/H$_2$O/CO$_2$(O$^\text{μ}$) + GB</td>
<td>$-17.4$</td>
<td>$-16.4$</td>
<td>$-3.7$</td>
</tr>
</tbody>
</table>

In the Cs$_8$Nb$_6$O$_{19}$/CO$_2$(O$^\text{c}$) isomer, where CO$_2$ interacts with a bridging oxygen, the C–O$^\text{c}$ bond distance is longer (calculated to be 1.44 Å) than the C–O$^\text{μ}$ bond distance in Cs$_8$Nb$_6$O$_{19}$/CO$_2$(O$^\text{μ}$), while the Cs–O$^\text{c}$ and Cs–O$^\text{μ}$ interactions are slightly stronger (based on the calculated Cs–O$^\text{c}$ and Cs–O$^\text{μ}$ distances). The above presented geometry parameters of Cs$_8$Nb$_6$O$_{19}$/CO$_2$(O$^\text{c}$) and Cs$_8$PONb/CO$_2$(O$^\text{μ}$) not only explain the calculated energy difference between these species, but are also consistent with the amounts of charge transfer from Cs$_8$Nb$_6$O$_{19}$ to CO$_2$: in the Cs$_8$Nb$_6$O$_{19}$/CO$_2$(O$^\text{c}$) and Cs$_8$Nb$_6$O$_{19}$/CO$_2$(O$^\text{μ}$) complexes, almost 0.8 |e| and 0.4 |e| negative charge is transferred from Cs$_8$Nb$_6$O$_{19}$ to CO$_2$, respectively. Furthermore, the putative CO$_2$–group in Cs$_8$Nb$_6$O$_{19}$/CO$_2$(O$^\text{c}$) has a total negative charge of 1.52 |e|.

The strong coordination of CO$_2$ to Cs$_8$Nb$_6$O$_{19}$ is also supported by IR spectroscopic studies, where the adsorption of CO$_2$ onto Cs$_8$Nb$_6$O$_{19}$ was investigated by recording the infrared spectra before, during, and after exposure of Cs$_8$Nb$_6$O$_{19}$ to a constant flux of CO$_2$. Upon adsorption of CO$_2$ on Cs$_8$Nb$_6$O$_{19}$, three prominent features appeared in the infrared spectrum (Fig. 2, i) at 1659 cm$^{-1}$, 1290 cm$^{-1}$ and 1229 cm$^{-1}$. Interestingly, we observed no feature in the infrared spectrum around 2300 cm$^{-1}$, which would be associated with a linear CO$_2$ molecule bound to the POM surface. The 1229 cm$^{-1}$ and 1290 cm$^{-1}$ bands are consistent with the IR-inactive symmetric stretch from the gas-phase ($v_1(C-O)$), which becomes IR active upon binding to the POM. The 1659 cm$^{-1}$ band is likely related to the antisymmetric $v_3(C-O)$ stretch of CO$_2$/CO$_3$ (occurs at 2349 cm$^{-1}$ in the gas-phase and significantly redshifts upon adsorption). The presence of both the $v_1$ and $v_3$ bands in the infrared spectrum indicates a bent structure of the adsorbate at the surface. Upon evacuation of CO$_2$ from the chamber, the 1229 cm$^{-1}$ spectroscopic feature diminishes, indicating that this band corresponds to the vibrational motion of weakly bound CO$_2$ species on the surface (Fig. 2, ii); however, the two other features (1659 and 1290 cm$^{-1}$) persist until annealing the Cs$_8$Nb$_6$O$_{19}$ sample at 423 K (Fig. 2, iii).

Fig. 1 Adsorption of the ambient gas molecules CO$_2$ and SO$_2$ on Cs$_8$Nb$_6$O$_{19}$ at the O$^\text{μ}$ sites (left) and bridging sites (right) with their important geometry parameters (in Å).

Fig. 2 Infrared spectra recorded during and after the adsorption of CO$_2$ onto Cs$_8$Nb$_6$O$_{19}$ at 300 K. (i) Adsorption of 100 mTorr of CO$_2$. (ii) After CO$_2$ evacuation. (iii) After CO$_2$ evacuation and thermal treatment at 423 K.
temperature required to fully remove the CO2 suggests that the molecules responsible for these infrared bands are strongly bound to Cs8Nb6O19. The experimentally observed IR features in the bending and asymmetric CO stretch motions of a bent CO2 molecule, are calculated to be 1316 and 1317 cm⁻¹ (for the band) and 1702 and 1719 cm⁻¹ (for the asymmetric stretch) in Cs8Nb6O19/CO2(Ot) and Cs8Nb6O19/CO2(Ot)², respectively. Thus, the above presented experimental and computational analysis shows that a large fraction of the adsorbed CO2 strongly binds to Cs8Nb6O19. Once at the surface, the molecule adopts a bent geometry, which activates the n vibrational motion toward absorption of infrared radiation.

(b) The geometric features of Cs8Nb6O19/ SO2(Ot) and Cs8Nb6O19/SO2(Ot)² adducts are similar to those of their CO2 analogs: among the interactions, the strongest are the S–O and S–O interactions, with 1.70 and 1.79 Å bond distances, respectively. These geometry parameters are consistent with the greater stability of the Cs8Nb6O19/ SO2(Ot) isomer. Furthermore, comparison of the calculated Cs8Nb6O19-X binding energies shows that SO2 interacts with Cs8Nb6O19 much more strongly, by nearly a factor of two, than CO2. However, both molecules clearly persist on the POM at ambient and well above ambient temperatures.

Further calculations showed that single Cs8Nb6O19 species can bind several CO2 and SO2 molecules. As seen in Table 2, where we have summarized the adsorption energies as a function of the number of molecules adsorbed at the six Ot sites, there is a pronounced monotonic convergence of the electronic and enthalpy binding energies up to n = 6. The free energies, on the other hand, reveal thermodynamic instability for CO2 adsorption at larger values of n, suggesting that only the Cs8Nb6O19/[CO2]₄ species with n = 4 are viable. The Cs8Nb6O19/[SO2]₃ species may still be stable for n > 6.

A2. Structure of Cs8Nb6O19 in the presence of NO2 radicals.

As one might expect, the interaction of Cs8Nb6O19 with NO2 radicals is conceptually different than those discussed above for the diamagnetic CO2 and SO2 molecules. Indeed, at first, in the gas-phase and at low temperatures, NO2 radicals are in equilibrium with dinitrogen tetroxide, N₂O₄, while higher temperatures shift the equilibrium towards nitrogen dioxide.²⁶

The calculations show that N₂O₄ is planar, with an N–N bond distance of 1.85 Å, which is significantly longer than the average N–N single bond length of 1.45 Å; this species has a dimerization energy of ΔE/ΔH/ΔG = 19.8/17.3/5.6 kcal mol⁻¹. Unlike NO2, N₂O₄ is diamagnetic and coordinates to the Cs8Nb6O19 catalyst (see Fig. 3) with a Cs8Nb6O19–N₂O₄ interaction energy of ΔE/ΔH/ΔG = −25.3/−25.3/−18.5 kcal mol⁻¹. Second, as shown in Table 2 and Fig. 3, the “free” NO2 radical (at ambient temperature) can interact with polyoxoniobate to form the [Cs8Nb6O19]/NO2 adduct. This adduct exists in two energetically stable isomeric forms, Cs8Nb6O19/NO2(Ot) and Cs8Nb6O19/NO2(Ot)², where the N atom of NO2 interacts with two Cs centers (with Cs¹–N and Cs²–N distances of 3.42 and 3.44 Å). To our surprise, these Cs–N interactions lead to electron transfer from Cs8Nb6O19 to NO2 in Cs8Nb6O19/NO2(Ot), as evidenced by population analysis: the calculated Mulliken spin/charge is NO2(Csn) = 0.34/−0.65 | e|. Thus, as a result of these interactions, almost 0.65 | e| charge is transferred from Cs8Nb6O19 to NO2; and, consequently, the Cs8Nb6O19 unit develops partial radical character. Further analysis shows that most of the unpaired spin of Cs8Nb6O19 is located on the internal O²⁻ center (−0.24 | e|) and the bridging O²⁻ (−0.14 | e|) located close to the Cs atoms coordinated to NO2, while the remaining spin is delocalized on all other atoms of the polyoxoniobate. Similarly, but to a lesser extent, NO2(Ot) has a 0.67/−0.41 | e| spin/charge distribution in the Cs8Nb6O19/NO2(Ot)² isomer. The calculated Cs8Nb6O19–NO2 binding energies are ΔH/ΔG = −22.2/−22.1 and −18.7/−13.9 kcal mol⁻¹ in Cs8Nb6O19/NO2(Csn) and Cs8Nb6O19/NO2(Ot), respectively.

Table 2 Adsorption of nX (X = CO2 and SO2 and n = 1 to 6) on Cs8Nb6O19 at its Ot-sites, reported as incremental ∆Zn–1(X) = Zn(X) = Zn(Cs8Nb6O19/X) − Zn−1(Cs8Nb6O19/X) − Z(X) energies (where Z = E, H or G) (in kcal mol⁻¹)

<table>
<thead>
<tr>
<th>n</th>
<th>X = CO2</th>
<th></th>
<th></th>
<th>X = SO2</th>
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<tr>
<td></td>
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<td>6.9</td>
<td>−29.0</td>
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Fig. 3 The calculated most energetically stable structures of NO2 and N₂O₄ adsorbed on Cs8Nb6O19, with their important geometry parameters (in Å).
Consequently, the acquired partial radical character of Cs$_8$Nb$_6$O$_{19}$/NO$_2$(Cs$^8$N) complex significantly increases its NO$_2$-affinity, enabling strong coordination of another (second) NO$_2$ radical to the O$^\cdot$-site of polyoxoniobate and formation of the most thermodynamically favorable Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] singlet species. The calculated energy of the reaction Cs$_8$Nb$_6$O$_{19}$/NO$_2$(Cs$^8$N) + NO$_2$ $\rightarrow$ Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] is $\Delta E/\Delta H/\Delta G = -53.8/-52.4/-35.9$ kcal mol$^{-1}$, while the energy of the reaction Cs$_8$Nb$_6$O$_{19}$/NO$_2$(O$^\cdot$) + NO$_2$ $\rightarrow$ Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] reaction is $\Delta E/\Delta H/\Delta G = -63.8/-61.5/-52.8$ kcal mol$^{-1}$ (see ESI for more details). Thus, removal of NO$_2$(O$^\cdot$) and/or NO$_2$(Cs$^8$N) from Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] with two NO$_2$-adsorbates requires greater energy than removing them from Cs$_8$Nb$_6$O$_{19}$/NO$_2$(O$^\cdot$) and/or Cs$_8$Nb$_6$O$_{19}$/NO$_2$(Cs$^8$N). The overall energy of the reaction Cs$_8$Nb$_6$O$_{19}$ + 2NO$_2$ $\rightarrow$ Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] is $\Delta E/\Delta H/\Delta G = -77.4/-74.6/-58.0$ kcal mol$^{-1}$ (see Table 1). To summarize, a relatively weak coordination of the first NO$_2$ radical to Cs$_8$Nb$_6$O$_{19}$ at the Cs sites promotes stronger coordination of the second NO$_2$ molecule at the O$^\cdot$ site of Cs$_8$Nb$_6$O$_{19}$. As a result, the coordination of the NO$_2$ radicals to Cs$_8$Nb$_6$O$_{19}$ is substantially stronger than that of CO$_2$, yet slightly weaker than that of one SO$_2$ molecule.

The reported highly stable Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] complex with two NO$_2$ fragments can also be formed via N–N bond activation of the coordinated N$_2$O$_4$ molecule by the polyoxometalate catalyst. The former pathway (i.e. stepwise addition of two NO$_2$ radicals to polyoxoniobate) may be valid at ambient temperature, while the latter process may occur at low temperature. In this paper, we did not study the N–N activation barrier; however, we found that the complex Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] (see Fig. 3) lies significantly lower in energy than the Cs$_8$Nb$_6$O$_{19}$ + N$_2$O$_4$ dissociation limit, by $\Delta E/\Delta H/\Delta G = 57.6/57.3/52.4$ kcal mol$^{-1}$, and $\Delta E/\Delta H/\Delta G = 37.8/40.0/46.8$ kcal mol$^{-1}$ lower than the Cs$_8$Nb$_6$O$_{19}$/N$_2$O$_4$ intermediate.

In order to better understand the factors impacting the strength of the Cs$_8$Nb$_6$O$_{19}$/NO$_2$ interaction, we also analyzed the geometry of the complex Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)]. As seen in Fig. 3, where we present the most important geometries of the Cs$_8$Nb$_6$O$_{19}$/NO$_2$(O$^\cdot$), Cs$_8$Nb$_6$O$_{19}$/NO$_2$(Cs$^8$N) and Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] species (for full geometries of these species, see the ESI$^\dagger$), in Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)], the Nb–O$^\cdot$ bond is elongated to 2.47 Å; concurrently, the Nb–O$^\cdot$N bonds (which are 2.34, 2.44 and 2.02 Å in these complexes, respectively) and N–O$^\cdot$ bonds (which are 1.28 and 2.25 Å in Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] and Cs$_8$Nb$_6$O$_{19}$/NO$_2$(O$^\cdot$), respectively) are formed. As a result, the complex Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] has one NO$_2$ fragment ($\delta = 0.4$) and one NO$_2$ fragment ($\delta = 0.94$) coordinated to the Cs-cations.

Above, we have shown that: (1) at ambient temperatures, a relatively weak coordination of the first NO$_2$ radical to Cs$_8$Nb$_6$O$_{19}$ confers partial radical character on the polyoxoniobate and promotes a stronger coordination of the second NO$_2$ radical to form a stable diamagnetic Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] complex, and (2) at low temperatures, coordination of a weakly stable N$_2$O$_4$ molecule to Cs$_8$Nb$_6$O$_{19}$ followed by facile N–N bond activation leads to the same Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] complex. Regardless of the formation mechanisms, in Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)], the coordination of the NO$_2$ radical positioned at O$^\cdot$ to Cs$_8$Nb$_6$O$_{19}$ is substantially stronger than that of CO$_2$, yet is slightly weaker than that of one SO$_2$ molecule.

These conclusions from our computations are fully supported by experiments. As with CO$_2$, the adsorption of NO$_2$ onto Cs$_8$Nb$_6$O$_{19}$ was probed with the use of infrared spectroscopy. Fig. 4 shows spectra for the interaction between NO$_2$ and Cs$_8$Nb$_6$O$_{19}$. The adsorption of NO$_2$ on the surface resulted in two infrared vibrational features – one at 1668 cm$^{-1}$ and another at 1240 cm$^{-1}$ (Fig. 4, i). These features are attributed to adsorbate N–O stretches as opposed to POM motions, which appear below 1000 cm$^{-1}$. Analysis of the calculated [Cs$_8$Nb$_6$O$_{19}$]–NO$_2$ complexes suggests that the 1668 cm$^{-1}$ feature is likely due to an asymmetric NO stretch originating from the Cs$_8$Nb$_6$O$_{19}$/N$_2$O$_4$ complex, which the calculations (unscaled) show to be at 1813 cm$^{-1}$. For the other NO$_2$ complexes, the highest frequency NO stretch is found below 1600 cm$^{-1}$, i.e. at a lower frequency relative to the experimental peak. Taking into account the usual anharmonic correction, these modes will be found to be even further redshifted to lower frequencies. However, if we consider that the calculated asymmetric (strongly IR active) NO stretch of a free NO$_2$ radical is 1752 cm$^{-1}$, and the known experimental value$^{25}$ is 1618 cm$^{-1}$, the resulting frequency scale factor of 0.92 brings the asymmetric NO stretch of the Cs$_8$Nb$_6$O$_{19}$/N$_2$O$_4$ complex to exactly 1668 cm$^{-1}$. Moreover, if the measured 1668 and 1240 cm$^{-1}$ peaks originate from the same thermal mixture of diamagnetic complexes, we expect that the 1240 cm$^{-1}$ peak, which persists at higher temperatures (Fig. 4, iii), is due to the Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] complex, which is much more stable to thermal perturbation than Cs$_8$Nb$_6$O$_{19}$/N$_2$O$_4$. The latter immediately transforms to Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] upon N–N activation by heating. Indeed, there is a group of IR-active NO stretching motions in the Cs$_8$Nb$_6$O$_{19}$/[NO$_2$(Cs$^8$N)NO$_2$(O$^\cdot$)] complex in the 1346 to 1361 cm$^{-1}$ (1238 to 1252 cm$^{-1}$ scaled) region, which captures the measured 1240 cm$^{-1}$ peak.
Thus, we present two spectra (shown in Fig. 5); one corresponds to low temperature, Fig. 5(A), which is the sum of Cs$_8$Nb$_6$O$_{19}$/N$_2$O$_4$ and Cs$_8$Nb$_6$O$_{19}$/[NO$_2$](Cs$^+$)NO$_2$(O$^-$)], and one corresponds to high temperature, Fig. 5(B), which is pure Cs$_8$Nb$_6$O$_{19}$/[NO$_2$](Cs$^+$)NO$_2$(O$^-$)]. The frequency axis is scaled by the same factor of 0.92. The calculation is consistent with experiments with regard to the disappearance of the 1668 cm$^{-1}$ peak and the persistence of the 1240 cm$^{-1}$ peak. However, the peak at 1470 cm$^{-1}$ (after scaling) in the calculated spectra, which is attributed to a local NO stretch of the NO$_3$ unit in Cs$_8$Nb$_6$O$_{19}$/[NO$_2$](Cs$^+$)NO$_2$(O$^-$)], is absent in the room-temperature experiments. This suggests that the formation of NO$_3$ requires a significant amount of thermal energy.

Furthermore, experiments clearly show that NO$_2$ is strongly bound to the POM, i.e. the 1240 cm$^{-1}$ peak is present even after gas phase evacuation (Fig. 4, ii) and upon heating the POM to 1470 K (Fig. 4, iii). In fact, thermal treatment up to 600 K was required to fully desorb the species, i.e. to remove NO$_2$ radicals. This suggests that NO$_2$ binds more strongly to the POM than CO$_2$, which is consistent with the computational data for the Cs$_8$Nb$_6$O$_{19}$/[NO$_2$](Cs$^+$)NO$_2$(O$^-$)] complex presented above (see Table 1 and the ESI†).

Thus, the data presented above show that in the presence of ambient gas molecules of CO$_2$, NO$_2$ and SO$_2$, Cs$_8$Nb$_6$O$_{19}$ will absorb these molecules more strongly than the water and GB molecules required for hydrolysis of Sarin (see Table 1). This is expected to impact the hydrolysis of Sarin by Cs$_8$Nb$_6$O$_{19}$ in the following two ways: first, because the ambient gas molecules coordinate to catalytically active O$^-$-centers, they block these catalytically active centers, hindering water and Sarin coordination, and may alter the previously reported mechanism of Sarin hydrolysis by Cs$_8$Nb$_6$O$_{19}$. Second, the interaction of an ambient gas molecule with Cs$_8$Nb$_6$O$_{19}$ may change the electronic properties of the polyoxoniobate: this is expected to only impact the calculated energetics of the Sarin hydrolysis and to not significantly change the nature of the previously reported intermediates and transition state structures.

Below, we test the first hypothesis by (a) studying the full potential energy surfaces of GB hydrolysis by Cs$_8$Nb$_6$O$_{19}$/X, where X = CO$_2$, SO$_2$, and (b) comparing these new findings with our previous results on the same reaction in the absence of ambient gas molecules. For the sake of simplicity, we discuss in detail only the reaction mechanism (as well as the structures of the pre-reaction complexes, intermediates, transition states and products) for X = CO$_2$ and compare these findings with those (previously reported) in the absence of ambient gas molecules. In addition, we briefly discuss, where appropriate, our findings for X = SO$_2$ (full potential energy surfaces are available in the ESI†). The reactivities of the NO$_2$ and other radical species coordinated to Cs$_8$Nb$_6$O$_{19}$ will be reported elsewhere.

### B. Hydrolysis of Sarin by Cs$_8$Nb$_6$O$_{19}$/X species (where X = CO$_2$ and SO$_2$)

As we have shown previously$^{24}$ and have briefly discussed above (see Scheme 1), Sarin hydrolysis by Cs$_8$Nb$_6$O$_{19}$ is a multistep process, with coordination of a water molecule to the catalyst as the first step. The calculations (see Table 1) show that coordination of H$_2$O to Cs$_8$Nb$_6$O$_{19}$ to form Cs$_8$Nb$_6$O$_{19}$/H$_2$O is exothermic/exergonic by (presented as ΔH$\Delta$G) 23.6/17.3 kcal mol$^{-1}$. In Cs$_8$Nb$_6$O$_{19}$/H$_2$O, the two hydrogens of the water molecule interact with one bridging (O$^-$) and one terminal (O$^+$) oxygen atom of the polyoxometalate.

Water molecule coordination to the adduct formed when CO$_2$ (or SO$_2$) binds to the O$^-$-center of Cs$_8$Nb$_6$O$_{19}$ is a few kcal mol$^{-1}$ less than that for “free” Cs$_8$Nb$_6$O$_{19}$; the energies are $^{−22.4/−11.9}$ and $^{−21.0/−9.7}$ kcal mol$^{-1}$ for X = CO$_2$ and SO$_2$, respectively. This effect is more pronounced for the Cs$_8$Nb$_6$O$_{19}$/SO$_2$ adduct than for Cs$_8$Nb$_6$O$_{19}$/CO$_2$. Furthermore, as seen in Fig. 6, the water coordination motif in Cs$_8$Nb$_6$O$_{19}$/CO$_2$/H$_2$O is different from that in Cs$_8$Nb$_6$O$_{19}$/H$_2$O: because CO$_2$ occupies the O$^-$-position in Cs$_8$Nb$_6$O$_{19}$/CO$_2$, the H$_2$O molecule is H-bonded to one bridging (O$^-$) and one CO (O$^+$) oxygen atom (instead of O$^-$). The calculated O$^-$–H$^+$ and O$^+$–H$^-$ bond distances are $^{1.76}$ and $^{1.85}$ Å, respectively.

Following the formation of the Cs$_8$Nb$_6$O$_{19}$/X/H$_2$O complex, the addition of Sarin to this intermediate occurs. Previously, we examined several approaches of Sarin to Cs$_8$Nb$_6$O$_{19}$ and found that nerve agent decomposition occurs when Sarin approaches the hydrated Cs$_8$Nb$_6$O$_{19}$ segment with its O(sp$^3$) and O(sp$^3$) atoms (labeled in Fig. 6 and below as O$^3$ and O$^1$, respectively)$^{24}$ The additional stabilization of the complex arises from the long-range O$^1$–Cs$^+$ ionic interaction. Thus, for the purposes of modeling the decomposition of Sarin in the presence of carbon and sulfur dioxide, it is sufficient to examine the most energetically favorable pathway, similar to that previously reported for the case with no ambient gas molecules. In keeping with the previously established shorthand notation, the pre-reaction complex of this reaction pathway is labeled as R–F–X.

The present calculations show that the coordination of Sarin (GB) to Cs$_8$Nb$_6$O$_{19}$/X/H$_2$O is exothermic by $^{−18.0/−2.4}$ and $^{−17.4/−3.8}$ kcal mol$^{-1}$ for X = CO$_2$ and SO$_2$, respectively. Inspection of the structure of the Cs$_8$Nb$_6$O$_{19}$/X/H$_2$O/GB, R–F–X, intermediate reveals a non-covalently bonded [Cs$_8$Nb$_6$O$_{19}$/CO$_2$/H$_2$O]–GB complex. For example, as seen in Fig. 6, in contrast to

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**Fig. 5** The calculated harmonic IR spectra (all in the NO stretch region), scaled by 0.92, of (A) the sum of the Cs$_8$Nb$_6$O$_{19}$/N$_2$O$_4$ and Cs$_8$Nb$_6$O$_{19}$/[NO$_2$](Cs$^+$)NO$_2$(O$^-$)] species; (B) the pure Cs$_8$Nb$_6$O$_{19}$/[NO$_2$](Cs$^+$)NO$_2$(O$^-$)] species.
the coordination of GB to Cs$_8$Nb$_6$O$_{19}$/H$_2$O, in Cs$_8$Nb$_6$O$_{19}$/CO$_2$/H$_2$O/GB, the nerve agent is coordinated to one of the Cs centers of the Cs$_8$Nb$_6$O$_{19}$-core with its P=O double bond. Several H-bonds also exist between the GB ligand and the [Cs$_8$Nb$_6$O$_{19}$/CO$_2$/H$_2$O]-fragment. In this complex, the calculated Cs–O$_4$ bond distance is 3.13 Å and the nascent P–O$_3$(OH$_2$) bond distance is 3.12 Å.

In the next step, hydrolysis of the coordinated water molecule occurs between the coordinated gas molecule X, the bridging oxygen (O$^m$) of the Cs$_8$Nb$_6$O$_{19}$-core and the phosphorus center of Sarin. The transition state associated with this process, TS-F_CO$_2$, is shown in Fig. 6 (for TS-F_SO$_2$, see the ESI‡). As seen in this figure, at TS-F_CO$_2$, the breaking O$_3$–H$_1$ bond of the water molecule is elongated to 1.16 Å, and the forming O$_m$–H$_1$ bond distance becomes 1.25 Å. In addition, Nb$^1$–O$^i$ and Nb$^2$–O$^i$ bonds are slightly elongated and the Cs$^3$–O$^i$ bond is slightly shortened. Importantly, the Cs$^3$-center of the Cs$_8$Nb$_6$O$_{19}$ core also interacts with the oxygen (O$^3$) of water and provides additional support for hydrolysis. Here, the other coordinates of interest are the P–O$_3$(H$_2$O) bond and the P–F bond.

As seen in Fig. 6, P–O$_3$(H$_2$O) undergoes a major reduction from 3.12 Å in R–F_CO$_2$ to 1.96 Å in TS–F_CO$_2$. Its P–F counterpart, located trans to the water-activated molecule, extends from the typical single bond in R–F_CO$_2$, with an increase from 1.62 Å to 1.71 Å in TS–F_CO$_2$. Similar geometry changes at the hydrolysis transition state were observed for X = SO$_2$ (see the ESI†). As seen in Fig. 7, the calculated $\Delta E/\Delta G$ barrier heights relative to R–F_X are 7.8/7.5 and 8.4/8.8 kcal mol$^{-1}$ for X = CO$_2$ and SO$_2$, respectively. These values are slightly larger than the values of 6.8/6.1 kcal mol$^{-1}$ calculated for the reaction in the absence of these ambient gas molecules; this suggests that common battlefield contaminants may impair the hydrolytic decomposition of nerve agents under operational conditions.

The hydrolysis product is a pentacoordinated-phosphorus complex P$_5$-F_X with a trigonal bipyramidal structure around the central phosphorus atom. In our previous paper, we showed that this intermediate exhibits multiple isomeric forms. Here, we discuss only the energetically most favorable form, which is directly connected to the transition state TS–F_X. For example,
as seen in Fig. 6, the formed P-O bond in P5-F CO2 contracts to 1.79 Å, while its P-F counterpart, located trans to the activated water molecule, extends to 1.76 Å. The broken O–H bond is elongated to 1.64 Å and the Nb1–O sp2 and Nb2–O sp3 bonds are elongated to 2.20 and 2.13 Å, respectively. Concurrently, the Cs3–O sp3 bond of 3.11 Å is formed to provide additional stabilization to the pentacoordinated-phosphorus complex, similar to that previously reported in P5-F.44 Based on the calculated Mulliken charge distribution, the resulting P5-F CO2 complexes can be labeled as a [[(GBOH)–(Cs8Nb6O19H/X)]] ion-pair system.

As shown in Fig. 7, the hydrolysis of Sarin, i.e. the reaction Cs8Nb6O19X + H2O → R-F X → TS-F X → P5-F X for X = none, CO2 or SO2, is exergonic by −50.1/−27.9, −38.8/−11.1 and −40.5/−14.7 kcal mol−1 (presented as ΔH/ΔG) and proceeds over energy barriers of 6.8/6.1, 7.5/7.5 and 8.4/8.8 kcal mol−1 (calculated relative to the pre-reaction intermediate R-F X), respectively. The reaction R-F X → TS-F X → P5-F X is exothermic for X = none and SO2 by 6.8/6.4 and 0.4/1.2 kcal mol−1, respectively, but is endothermic by 3.4/3.2 kcal mol−1 for X = CO2. These energy values allow us to conclude that the presence of ambient gas molecules increases the energies of the stationary points relative to the asymptote of the reactants. This is likely the result of a different charge distribution on Cs8Nb6O19X relative to Cs8Nb6O19, where X acquires a net negative charge of 0.8 to 0.7 [e], as we showed above. Furthermore, X coordinates to the O active center and disables its hydrolytic activity. The presence of ambient gases increases the hydrolysis barrier by 1.0 to 2.5 kcal mol−1, and this change in the energy barrier is closely associated with the Cs8Nb6O19X complexation energy: the stronger the Cs8Nb6O19−X bond, the higher the barrier for Sarin hydrolysis.

C. Pentacoordinated P5-F X intermediate dissociation

Once the pentacoordinated P5-F X species is formed, the reaction can proceed along several paths, as discussed in our previous paper.44 In order to evaluate the role of the catalyst in the course of the reaction, as above, here we discuss in detail only those pathways that directly involve the catalyst. These are the HF and isopropanol elimination and, ultimately, desorption pathways. The accompanying products of these paths are isopropyl methyl phosphonic acid (i-MPA) and methyl phosphonofluoridic acid (MPFA), respectively. It is evident that in order to form HF or isopropanol, protonation of the fluoride or oxygen centers of the isoproxy ligand is required. Furthermore, in order to facilitate regeneration of the catalyst, the ultimate proton source should be the O4H group of the [Cs8Nb6O19H/X] cation. However, these processes are expected to be very complex and may proceed via multiple mechanisms. One of these processes could involve several water molecules, which are expected to be present in real experimental conditions. In this mechanism, a water molecule located close to the fluoride or oxygen atoms of the isoproxy ligand is expected to donate its proton to these groups (to form HF and/or isopropanol, respectively) and compensate by removing the proton from the O4H group of the catalyst via a H-bonding network. This process depends on multiple factors (including, but not limited to, the concentration of water in the system and the reaction temperature) and was not studied in this paper.

Another possible mechanism of HF and/or isopropanol formation is direct removal of the proton from the O4H group of the catalyst by the fluoride and/or isopropoxide ligands, respectively. As shown previously for the Cs8Nb6O19 catalyst (i.e., in the absence of ambient gas molecules),45 these processes occur with very small energy barriers which have no contribution to the overall outcome of the decontamination reaction but lead to the most energetically stable intermediates, Cs8Nb6O19−(i-MPA)−HF and Cs8Nb6O19−(MPFA)−(i-POH), respectively (see Fig. 8). Here, we performed an extensive search to locate the transition states TS2-F_HF_X and TS2-F_(i-POH)_X that lead to either HF and i-MPA or isopropanol (i-POH) and MPFA from the most stable pentacoordinated intermediate P5-F X (where X = CO2 or SO2). Ultimately, we were able to locate only the TS2-F_(i-POH)_X transition state (see Fig. 8). The search for the HF formation transition state TS2-F_HF_X was unsuccessful and always led to either the Cs8Nb6O19−(i-MPA)−HF intermediate, its derivative F−⋯−H−⋯−O4H intermediate, or the pre-reaction complex P5-F_X. For example, in Fig. 8, we present the intermediates, transition states and products involved in pentacoordinated P5-F CO2 intermediate dissociation alone, with their important geometry parameters (for those of X = SO2, see the ESI†). The relative energies of these species, calculated from the P5-F_X pre-reaction complex, are given in Fig. 9.

As seen in Fig. 8, at the transition state TS2-F_(i-POH)_CO2 associated with the formation of i-POH and MPFA, the activated P-O sp3 bond extends to 2.19 Å from 1.68 Å in P5-F CO2, with simultaneous formation of a double H-bond network (O3−H1 = 1.63 Å and O4−H2 = 1.57 Å) as a precursor to the

![Fig. 8](Image Link) The calculated transition states, intermediates and products of the dissociation of pentacoordinated P5-F CO2 (i.e. reactions: P5-F CO2 → Cs8Nb6O19/CO2-(MPFA)-(i-POH) → Cs8Nb6O19/CO2 + MPFAH + (i-POH) and P5-F_X → Cs8Nb6O19/CO2-(MPA)-HF → Cs8Nb6O19/CO2 + MPAH + HF) with their important geometry parameters (in Å). Similar structures for X = SO2 are presented in the ESI†.
charge-preserving double proton transfer. In other words, as the proton of the O3H+ group moves to Sarin, the proton on the POH group of Sarin migrates back to the Cs8Nb6O19/X-core to form [HXOt]q, where X = CO2. As a result, the formed P–O(1) and H2O bond is shortened from 1.79 Å in P5–F–CO2 to 1.61 Å in the transition state.

As seen in Fig. 9, the calculated energy barriers from P5–F–X are 7.0/7.6, 5.4/5.4 and 3.6/6.5 kcal mol−1 for X = none, CO2 and SO2. Thus, the presence of these gas molecules in the reaction mixture slightly reduces the pentacoordinated P5–F–X intermediate dissociation barrier (by 2 to 4 kcal mol−1). Furthermore, the changes in the i-POH and MPFA formation energy barriers correlate with the Cs8Nb6O19/X complexation energy: the stronger the Cs8Nb6O19/X bond, the smaller the i-POH and MPFA formation energy barriers.

Comparison of the calculated energetics for the dissociation of the pentacoordinated intermediate with those for hydrolysis (i.e. formation of the pentacoordinated intermediate) show that, in general, the hydrolysis step is a rate-determining step for all reported species, and the presence of ambient gas molecules increases this energy barrier only slightly, by 2 to 4 kcal mol−1. Furthermore, the height of this rate-determining energy barrier correlates with the Cs8Nb6O19/X complexation energy: the stronger the Cs8Nb6O19/X bond, the more difficult the hydrolysis of GB by the Cs8Nb6O19 catalyst.

D. Catalyst regeneration

Thus, the facile dissociation of the P5–F–X species, as reported previously for P5–F, yields HF and i-MPA and/or i-POH and MPFA products. All these species are initially bound to Cs8Nb6O19, as shown in Fig. 8 for X = CO2 and the EST‡ for X = SO2. For example, in the Cs8Nb6O19/CO2-(i-MPA)-HF complex, the (i-MPA)-fragment forms a hydrogen bond with the O2 and OH-unit of the HOCO2 fragment, respectively. The HF molecule, on the other hand, in the presence of an X molecule, prefers to form an [F–···H+] ion-pair prior to dissociation. Similarly, in the Cs8Nb6O19/CO2-(MPFA)-(i-POH) complex, the (i-POH) molecule and MPFA-fragment are hydrogen bonded to another O atom and the OH-unit of the HOCO2 fragment, respectively: the calculated H3–O6 and O3–H2 bond distances are 1.73 and 1.67 Å, respectively. In addition, there are electrostatic interactions between the O center of the isopropanol molecule and two Cs cations of the Cs8Nb6O19/CO2 core, with Cs1–O3 and Cs1–O2 bond distances of 3.19 Å and 3.31 Å, respectively. The formed P–O3 fragment also interacts with the Cs1-center, with a Cs1–O3 distance of 3.16 Å.

As seen in Fig. 9, the formed Cs8Nb6O19/X-MPFA-(i-POH) is the energetically lowest structure on the potential energy surface of the entire GB hydrolysis and decontamination reaction by Cs8Nb6O19 both in the absence and presence of ambient gas molecules. The intermediate Cs8Nb6O19/X-(i-MPA)-HF is found to be only slightly higher in energy. As we mentioned previously,24 the high stability of these intermediates is due in part to the strong hydrogen bonds between the adsorbates and the Cs8Nb6O19/X-core; however, it is also due to the additional stabilizing interactions between the Cs counter-ions and the electronegative atoms of the nerve-agent fragments.

Desorption of HF and isopropanol from Cs8Nb6O19/X-(i-MPA)-HF and Cs8Nb6O19/X-MPFA-(i-POH) requires 15.2/12.7 and 20.0/5.3 kcal mol−1 energy, respectively, for X = CO2. Dissociation of HF and isopropanol only slightly modifies the geometries of the products Cs8Nb6O19/X-(i-MPA) and Cs8Nb6O19/X-MPFA fragments (for example, see Fig. 8 for X = CO2) compared with the Cs8Nb6O19/X-(i-MPA)-HF and Cs8Nb6O19/X-MPFA-(i-POH) adducts; therefore, this will not be discussed in detail.

However, both i-MPA in Cs8Nb6O19/X-(i-MPA) and MPFA in Cs8Nb6O19/X-MPFA are strongly bound to the protonated [Cs8Nb6O19/X]H+ core. Thus, regeneration of the catalyst requires deprotonation of the [Cs8Nb6O19/X]H+ core and protonation of the phosphonic acids i-MPA and MPFA. This step of the reaction, which forms a final decontaminated form of the GB and re-generated catalyst, is found to be highly endothermic/endergonic, i.e. 6.4/6.5 and 2.8/1.9 kcal mol−1 for i-MPAH and MPFAH formation, respectively. Overall, the last steps of the reaction, i.e. the reactions Cs8Nb6O19/X-(i-MPA)-HF → Cs8Nb6O19/X + HF + (i-MPAH) and Cs8Nb6O19/X-MPFA-(i-POH) → Cs8Nb6O19/X + (i-POH) + MPFAH, are highly prohibitive and require energies of 80.3/60.2 (X = none), 64.4/63.6 (X = CO2), and 66.0/39.4 (X = SO2) kcal mol−1 and 81.0/60.4 (X = none), 71.2/43.6 (X = CO2), and 63.3/36.4 (X = SO2) kcal mol−1, respectively. Furthermore, deprotonation of the [Cs8Nb6O19/X]H+ core and protonation of the phosphonic acids i-MPA and MPFA is expected to be very complex and may proceed via several pathways depending on the reaction conditions. One of these may involve any surrounding water molecules, in real experimental conditions, via a concerted protonation-deprotonation mechanism involving the hydrogen-bonded water-based network. However, this process depends on multiple factors (including, but not limited to, the concentration of water in the system and the reaction temperature) and was not studied in this paper. We also failed to locate a transition state associated with the direct deprotonation of...
Conclusions

This paper, for the first time, addresses the impact of environmentally-significant ambient gas molecules, NO₂, CO₂ and SO₂, on the structure, stability and decontamination activity of a basic polyoxometalate species. Specifically, Cs₈Nb₆O₁₉ in the presence of these gases has been studied in depth by complementary computational and experimental approaches. It was found that:

(1) Cs₈Nb₆O₁₉ absorbs ambient gas molecules of X = CO₂, NO₂ and SO₂ more strongly than it absorbs water or Sarin (GB) molecules. The calculated Cs₈Nb₆O₁₉-X binding energy follows the trend for ΔG(X = CO₂) < ΔG(NO₂) < ΔG(SO₂).

(2) The impacts of the diamagnetic CO₂ and SO₂ molecules on polyoxoniobate Cs₈Nb₆O₁₉ are fundamentally different than that of the NO₂ radical. At ambient temperatures, weak coordination of the first NO₂ radical to Cs₈Nb₆O₁₉ confers partial radial character on the polyoxoniobate and promotes a stronger coordination of the second NO₂ radical to form a stable diamagnetic Cs₈Nb₆O₁₉(NO₂)₂ species; meanwhile, at low temperatures, NO₂ radicals form weakly stable dinitrogen tetraoxide (N₂O₄), which interacts weakly with Cs₈Nb₆O₁₉.

(3) Similar to the case without ambient gas molecules, reported previously,²⁴ in the presence of X, GB hydrolysis by Cs₈Nb₆O₁₉/X proceeds via general base hydrolysis involving: (a) adsorption of water and the nerve agent on the Cs₈Nb₆O₁₉/X catalyst, (b) concerted hydrolysis of the adsorbed water molecule on a basic oxygen atom of the polyoxoniobate and nucleophilic addition of the nascent OH group to the phosphorus center of the nerve agent, (c) rapid reorganization of the resulting pentacoordinated-phosphorus intermediate followed by dissociation of either HF or isopropanol with formation of POM-bound isopropyl methyl phosphonic acid (i-MPA) or methyl phosphonofluoridic acid (MPFA), respectively.

(4) Cs₈Nb₆O₁₉ adsorbs ambient gas molecules X at its basic O¹ (or O¹') reactive centers, which shields them from involvement in the base hydrolysis. As a result, one of the O centers of the coordinated ambient gas molecule becomes an active hydrolysis center. This increases the energies of the stationary points relative to the asymptote of the reactants and increases the hydrolysis barrier. These changes are closely correlated with the Cs₈Nb₆O₁₉-X complexation energy; the stronger the Cs₈Nb₆O₁₉-X bond, the higher the barrier for Sarin hydrolysis.

(5) The most energetically stable products of the GB hydrolysis and decontamination reaction are Cs₈Nb₆O₁₉/X-MPFA-(i-POH) and Cs₈Nb₆O₁₉/X-(i-MPA)-HF both in the absence and presence of ambient gas molecules. The high stability of these intermediates is due in part to the strong hydrogen bonds between the adsorbates and the protonated [Cs₈Nb₆O₁₉/X/H⁺]⁺ core and to interactions between the Cs counterions and the electronegative atoms of the adsorbates.

(6) Desorption of HF or/and (i-POH) and regeneration of the catalyst requires deprotonation of the [Cs₈Nb₆O₁₉/X/H⁺]⁺-core with protonation of the phosphonic acids i-MPA and MPFA. Regeneration of the catalyst is a highly exergonic process and is the rate-limiting step for GB hydrolytic decontamination, both in the absence and presence of ambient gas molecules.

Notes

A. Computational and experimental procedures

A1. Computational methodology. A major computational challenge in the present work is to properly describe the non-covalent interactions involving the various ions in the systems studied: the Cs⁺ counter-cations, [Nb₆O₁₉]⁸⁻; with its large negative charge, and the H⁺ and OH⁻ ions resulting from heterolytic water dissociation. These interactions are expected to be well described by the M06-L density functional,²⁵ a pure density functional designed for transition metal bonding and non-covalent interactions. Therefore, all presented calculations have been carried out with the M06-L density functional, as implemented in the Gaussian09 code.²⁶ In these calculations, we used the 6-31++G(d,p) basis set for the elements S, P, F, O, C, H and the Lanl2dz basis set with corresponding Hay–Wadt effective core potentials for Nb and Cs, as implemented in Gaussian09. The sets of diffuse functions (+) were added specifically to obtain proper descriptions of the diffuse charge densities and long-range interactions. All reported stationary points were confirmed to have either all real frequencies (minima) or one imaginary frequency (transition states). The latter were further verified to connect the corresponding minima by IRC calculations. All reported enthalpy and Gibbs free energies were computed at a temperature of 298.15 K and 1 atm pressure.

A2. Experimental methodology. The synthesis of Cs₈Nb₆O₁₉-14H₂O followed a known literature procedure. A solution of cesium hydroxide (14.6 g, 50% by weight) was heated to 90 °C in an Erlenmeyer flask. 5 g of hydrous, amorphous niobium oxide was added in small portions, with full dissolution of each portion before addition of the subsequent portion. Evaporative crystallization yielded giant hexagonal crystals.

Infrared spectroscopic experiments were performed in a stainless-steel high-vacuum chamber with a base pressure of ~1 × 10⁻⁸ Torr. The Cs₈Nb₆O₁₉ sample was pressed, as a 7 mm diameter disk, into a tungsten grid, which was then clamped onto a sample mount coupled to a precision manipulator. An empty region of the grid was used to monitor the gas phase species in the chamber and was also employed as a background for surface adsorption and desorption studies. The grid was resistively heated, and the temperature was monitored via a K-type thermocouple spot-welded adjacent to the sample. A PID controller mediated the sample temperature to within ±1 K. Details of the vacuum chamber and sample mount can be found in a previous publication.²⁷ An FTIR spectrometer (Thermo, Nicolet, Nexus 470 FTIR) with an external liquid-N₂-cooled MCT-A detector and a spectral resolution of 2 cm⁻¹ was used for collection of the infrared spectra.
Conflicts of interest

There are no conflicts to declare.

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Notes and references


