Ab Initio Reaction Energetics of Phosgene Decomposition by Zn^{2+} and Ni Atoms: Implications for Gas Mask Filters†

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The reactions of phosgene, a World War I-style chemical weapon, with two transition metals (TMs) are examined by complete active space self consistent field and multireference single and double excitation configuration interaction theory. We clarify the reason why TM ions are effective at decomposing phosgene yet do not react catalytically. In particular, we find that phosgene reacts much more exothermically with Zn^{2+}, an ion present in protective mask filters, than with the isoelectronic neutral TM case of Ni. Zn ions react by three barrierless, extremely exothermic routes, with oxidative cleavage of C−Cl bonds as the most favored. By contrast, we find the isoelectronic Ni atoms undergo only C−Cl bond insertion. The predicted reaction energetics can be nicely rationalized within a valence bond view of oxidation states and organometallic bonding. These energetics then are used to give a chemical reason why saturation of the charcoal filters occurs.

Introduction

World War I (WWI)-style chemical weapons still pose a serious threat to human beings. This is because activated charcoal filters used in protective gas masks become saturated more easily by these chemicals than by the more potent nerve and mustard agents.[1] High oxidation state transition metal (TM) ions are impregnated in the porous carbon networks of these filters.[2] It is known that these ions are the critical players determining the ability of the filters to prevent breakthrough of WWI-type chemical warfare agents, namely cyanogen chloride (ClCN), phosgene (Cl_2CO), and hydrogen cyanide (HCN).[3] The effectiveness of these TM ions has been found empirically; almost nothing is known at the atomic level of the mechanism by which these TM ions react with the chemical agents, nor is the microscopic environment of the TM ions known. In order to understand why the gas mask filters saturate, we sought to uncover microscopic mechanisms by which the TM ions interact with chemical warfare agents. Elucidating these mechanisms may lead to a general understanding of the filter saturation phenomenon as well as how it might be delayed.

We have chosen to focus our study on the destruction of phosgene by TM ions, since it has not been studied extensively by experiment. All three of the WWI agents mentioned above are classified as acid-forming gases, since they react with water to form HCl (in the case of phosgene and cyanogen chloride) or they simply ionize in water (in the case of hydrogen cyanide). Under humid conditions (at night or in humid environments), the decomposition of these agents generally involves hydrolysis with subsequent neutralization of the acid via the added TM ions.[2] In the case of phosgene, CO_2 is a byproduct of the hydrolysis step, while HCl is thought to be neutralized by copper or zinc ions, probably present as oxides, to regenerate water and leave behind metal halides. In conditions of excess water, the acid simply remains dissolved in the water.

Humid conditions are *not* the focus of this study. Instead we are interested in conditions where little water is present, such as during the daytime in the arid deserts of the Middle East. Under such conditions, it is known that phosgene adsorbs on the activated, impregnated carbons both by physical adsorption as well as irreversible chemisorption,[4] where the latter is thought to involve reactions with the TM ions. Some of the TM ions currently used in the filters are: Mo^{6+}, Ag^{+}, Zn^{2+}, and Cu^{2+}.[1] Though a variety of counterions have been used to prepare the activated carbons, the environment of the TM cations in the final carbon product is not well characterized.

It is likely that filter saturation is due to *stoichiometric* (i.e., noncatalytic) chemistry where the ions get tied up with decomposition products. We wish to check this hypothesis in the current work, by characterizing at the atomic level how TMs decompose these toxic gases. Ultimately, one hopes to tailor the choice of TM or its environment so as to make the reactions catalytic. If a catalytic pathway could be found, the useful lifetime of the filters might be extended dramatically.

This study represents the first *ab initio* theoretical effort to understand the reaction energetics of chemical warfare agents with the TM ions present in activated charcoal filters. Since neither the structure of the carbon pores nor the local chemical environment of the TM ions are known, in this first work we consider simply the intrinsic reaction energetics of phosgene, Cl_2CO, interacting with isolated Zn^{2+} ions. To understand a bit about the special role played by *ions* in this reaction, we also carried out calculations of the reaction of phosgene with an isoelectronic, neutral TM, namely Ni atom. Obviously, the assumption made in these calculations is that the reaction takes place at isolated TM sites and that the carbon matrix plays no role. This is a less drastic assumption than one might otherwise presume, because it is known that phosgene and these other WWI gases do not react with the carbon matrix in the absence of these TM ions. We view the reaction chemistry presented herein as the simplest possible mechanistic pathways that might be occurring.

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† It is a pleasure to honor W. A. Goddard, III, by presenting this work that uses GVB ideas to rationalize the results.

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TABLE 1: CASSCF Structures (Å and Deg) of Phosgene and its Decomposition Products Formed by Reaction with Zn(II) and Ni(0): Experimental Values Shown in Parentheses

$Cl_2C{=}O$ (phosgene) planar, C_{2v}	$[Cl_2ZnCO]^{2+}$ planar, C_{2v}	$[ClCO]^+$	$[ZnCl]^+$	$Zn^{2+}(O{=}CCl_2)$ planar, C_{2v}	Cl_2NiCO planar, C_{2v}
C−O: 1.176 (1.1756)[a]	C−O: 1.129	C−O: 1.114	Zn−Cl: 2.132 (∼2.24)[b]	C−O: 1.258	C−O: 1.136
C−Cl: 1.738 (1.7381)[a]	Zn−C: 2.140	C−Cl: 1.629		C−Cl: 1.699	Ni−C: 2.385
	Zn−Cl: 2.454			Zn−O: 1.843	Ni−Cl: 2.193
∠O−C−Cl: 124.1°	∠O−C−Zn: 180°	∠O−C−Cl: 180.0°		∠Zn−O−C: 180.0°	∠O−C−Ni: 180.0°
∠Cl−C−Cl: 111.80° (111.83°)[a]	∠Cl−Zn−Cl: 112.0°			∠Cl−C−Cl: 119.30°	∠Cl−Ni−Cl: 167.4°
	∠C−Zn−Cl: 124.0°			∠O−C−Cl: 120.3°	∠C−Ni−Cl: 96.4°

[a] Nakata, M.; Fukuyama, T.; Kuchitsu, K.; Takeo, H.; Matsumura, C. *J. Mol. Spectrosc.* **1980**, *83*, 118. [b] Maeda, M.; Ito, T.; Hori, M.; Johansson, G. *Z. Naturforsch. A* **1996**, *51*, 63. This is an averaged value from Raman spectra of $ZnCl_2$ and $[ZnCl]^+$.

Theoretical Method

For phosgene, we used the Dunning/Huzinaga valence double-ζ basis set[5,6] for carbon and oxygen and included polarization functions ($\zeta_d = 0.64$ for carbon and $\zeta_d = 0.95$ for oxygen) and one set of s and p diffuse functions for oxygen ($\zeta_s = 0.088$ and $\zeta_p = 0.06$). Chlorine's 10 core electrons were represented by an effective core potential (ECP)[7] while the valence electrons were described using a double-ζ basis set[7] with a polarization function ($\zeta_d = 0.6$), and a set of s and p diffuse functions ($\zeta_s = \zeta_p = 0.049$). The core electrons of zinc and nickel were represented by the Los Alamos 18-electron ECP's[8] while the valence electrons were described using the Los Alamos valence double-ζ basis set.[8]

We carried out Hartree−Fock (HF), generalized valence bond with perfect pairing (GVB−PP)[9] using 5 correlated pairs, complete active space self-consistent field (CASSCF)[10] of 10 electrons in 10 orbitals, and multireference single and double excitation configuration interaction (MRSDCI) calculations for phosgene interacting with Zn^{2+} and Ni.

To adequately describe all of the reaction paths for phosgene and the TM's, a 10 orbital, 10 electron CAS was found to be necessary. In order to maintain a consistent orbital description, a choice was made to study only the singlet potential energy surface. This is well justified because phosgene, Zn^{2+} and all the three of its products are singlets. In the nickel case, while the Cl_2NiCO product is singlet, the nickel ground state is s^2d^8 (^3F). However, the excited s^1d^9, singlet state (^1D) is only 0.25 eV higher than the ground state. We will consider this small promotional cost to form ^1D Ni in the analysis of our results. For phosgene, the orbitals involved in the CAS were the bond orbitals (2 C−Cl σ/σ^*, 1 C−O σ/σ^*, 1 C−O π/π^*) and for Zn^{2+}, one d-lone pair was correlated. This approach was maintained through the calculations of all reaction paths. In the Ni + phosgene reaction, the open shell d-electrons on ^1D Ni are contained in the CAS active space. In the product Cl_2NiCO, five bonds are correlated within the CASSCF treatment: 2 Ni−Cl σ/σ^*, a Ni−C donor/acceptor σ/σ^*, and C−O σ/σ^* and π/π^*. All CASSCF energy and gradient calculations were performed using the program HONDO.[11] Initial guesses for the CASSCF calculations come from GVB−PP calculations, which were found to be optimal initial guess choices for CASSCF calculations.[12]

All calculations were performed using no symmetry constraints to minimize bias in the geometry optimization and saddle point searches. The optimal structures for the reaction paths of Zn^{2+} or Ni + phosgene were determined using the quasi-Newton[13] method, and TSs for all paths were searched for using the DIIS-Ridge method.[14] Both methods used CASSCF(10 electrons/10 orbitals) energies and analytic gradients. The structures were considered converged when the gradient components of all movable atoms were minimized to below 5×10^{-4} au. To determine the final energetics, MRSDCI[15] calculations were performed on all the optimized reaction structures. The reference space for the MRSDCI contained all configuration state functions (CSF's) in the 10 electrons in 10 orbitals CAS with coefficients ≥ 0.01 for all cases except Cl_2ZnCO^{2+}, where we used all CSF's with coefficients ≥ 0.065 in order to keep the MRSDCI to a manageable size. Up to ≈6 million configuration state functions were used in these calculations.

Results and Discussion

Equilibrium Structures. The CASSCF equilibrium structures for each reactant and product of each reaction pathway found are collected in Table 1. As noted below, each reaction path is so exothermic that no barriers were found on the potential energy surfaces and hence there are no transition state structures to report. To the best of our knowledge, of these species only the structures of phosgene and $ZnCl^+$ are known experimentally. The CASSCF structures for these two molecules are in excellent agreement with experiment.[16,17] One can also understand the trends observed in the structures as follows. Notice that the C−O bond is shortest (1.114 Å) in $ClCO^+$, indicative of a triple bond, as one would expect from a valence bond view of this molecular ion.[18] In particular, one would ascribe sp hybridization to the C^+ ion, such that a covalent C−Cl bond is made between a C^+ sp hybrid and a Cl p orbital, a covalent C−O sigma bond is formed between the other C^+ sp hybrid and a singly occupied oxygen p orbital, a covalent C−O pi bond is comprised of singly-occupied C p−π and O p−π orbitals, and a donor-acceptor π-orbital comprised of oxygen's doubly-occupied p-orbital donating into the C^+'s empty p−π orbital makes up the triumvirate of bonds between oxygen and carbon.[19] The C−O bonds in the carbonyl complexes $[Cl_2ZnCO]^{2+}$ and Cl_2NiCO are slightly longer than in $ClCO^+$, presumably due to the perturbations of CO 5σ donation/dπ-pπ backbonding that lengthen the CO bond slightly.[20] Phosgene and phosgene Lewis-acid-complexed to Zn^{2+} have the longest C−O bonds, in the traditional region for C−O double bonds. The zinc complexation reduces the electron density of the phosgene in the region of the C−O bond, resulting in a reduced bond order and hence a slightly longer bond. The C−Cl bond lengths follow expected trends as well: the sp^2-hybridized C orbital in phosgene (or Zn-complexed phosgene) binds chlorine more loosely than the sp-hybridized C in $ClCO^+$. Finally, note the distinct difference in the Cl-M-Cl bond angles for the two Cl_2MCO complexes. For M = Ni, the bond angle is near linear, which is consistent with Ni(0)'s s^2d^8 ground state producing sp hybrids that are near linear, while for M = Zn^{2+}, its d^{10} ground state mixes in

TABLE 2: Phosgene + Zn^{2+} or Ni Reaction Energetics at the CASSCF/MRSDCI level: Total Energies Given in Atomic Units (hartrees)

		theory	total energy (au)	Δ*E*(Products−Reactants) (kcal/mol)
		Phosgene + Zn^{2+} Reaction		
reactants	phosgene + Zn^{2+}	CASSCF (10/10)	−205.034 36	
		MRSDCI	−205.103 59	
product 1	$[Cl_2ZnCO]^{2+}$	CASSCF (10/10)	−205.183 35	
		MRSDCI	−205.210 64	
			(MRSDCI)	−67.2
product 2	$Zn^{2+}(O{=}CCl_2)$	CASSCF (10/10)	−205.161 31	
		MRSDCI	−205.234 36	
			(MRSDCI)	−82.0
products 3	$Cl{-}C{\equiv}O^+$	CASSCF (6/6)	−127.249 01	
		MRSDCI	−127.322 39	
	$Zn^+{-}Cl$	CASSCF (4/4)	−78.044 10	
		MRSDCI	−78.058 44	
			(MRSDCI)	−174.0
		Phosgene + Ni(^{1}D) Reaction		
reactants	phosgene + Ni	CASSCF(10/10)	−181.386 15	
		MRSDCI	−181.476 29	
product	Cl_2NiCO	CASSCF(10/10)	−181.538 23	
		MRSDCI	−181.632 29	
			(MRSDCI)	−97.9

s character into the Zn−Cl bonds in a more limited fashion, resulting in a small Cl−Zn−Cl angle.

Reaction Energetics. The equilibrium total energies of each species and the energetics for various pathways are summarized in Table 2. Our CASSCF/MRSDCI calculations for Zn(II) reactions reveal unusual new chemistry. Given that Zn(II) is a d^{10} ion, one would have thought that perhaps the only reaction that could occur is a Lewis acid complex of Zn(II) to a phosgene lone electron pair. Quite the contrary: we find that although C−Cl bonds are known to be very strong, these bonds are readily ripped apart, releasing so much energy in the process that Zn(II) cannot act as a catalyst and is in fact poisoned to further reaction. This may explain the more facile saturation of the filters toward agents containing C−Cl bonds.

In particular, for Zn(II) reacting with phosgene we find three exothermic pathways, as shown in Figure 1. In order of increasing exothermicity, they are: (i) cleavage of both C−Cl bonds to form $Cl_2Zn(CO)^{2+}$, (ii) formation of a very strong Lewis acid−Lewis base adduct in which phosgene coordinates to the zinc ion via an O lone pair but does not break any bonds, and (iii) oxidative cleavage of one C−Cl bond—effectively a chloride ion transfer—to form $ZnCl^+$ and $ClCO^+$. We find at the MRSDCI level, that all pathways are highly exothermic (by 67-174 kcal/mol). The trends in the exothermicity can be rationalized within a valence bond (VB) view of oxidation states[20] as follows. Pathway (i) is the least exothermic because ground state d^{10} Zn^{2+} is closed shell and therefore must mix in the s^1d^9 excited state (~10 eV higher!) in order to form covalent bonds to the chlorines. This necessarily weakens the Zn−Cl bonds and lowers the exothermicity. Pathway (ii) is intermediate because it involves no promotion of the zinc ion, no C−Cl bonds are broken, and yet only one donor-acceptor Zn−O bond is formed. Pathway (iii), on the other hand, breaks one C−Cl bond but in return produces both a Zn−Cl bond and a C−O triple bond which is exceedingly strong. This is the source of the great exothermicity of the last pathway.

One may ask, why doesn't the cleavage reaction in pathway (iii) involve neutral Cl transfer to form ClCO and $ZnCl_2^+$? The simple answer is that $ZnCl_2^+$ would involve only a weak ion-induced dipole interaction and thus the reaction is highly endothermic (having lost a very strong C−Cl bond). Transfer of chloride ion allows very strong bonds to form, as mentioned above.

In all three cases, the large exothermicity is responsible for the noncatalytic nature of the reaction, since these pathways are dead ends for the Zn ion. Furthermore, after the $Zn{-}Cl^+$ species ties up one Zn ion, it is likely that another Zn ion may be involved in breaking down the ClCO+ species, to form $ZnCl^+$ and probably CO_2 (if the carbonyl reacts with oxide ions likely to be present in the actual charcoal filter). Extensive saddle point search calculations found no transition states or intermediates and no barriers along any of the reaction paths. Given the large exothermicity of each of these reactions, this is not particularly surprising, based on the Hammond postulate.[21]

The chemistry of Ni with phosgene is much simpler. Despite an exhaustive search of various relative orientations of phosgene and Ni, we found that phosgene always decomposed directly via oxidative addition to $Ni(CO)Cl_2$. We predict that this is a very exothermic reaction (by 98 kcal/mol). Similar to the case of zinc ion, saddle point search calculations found no transition state and no intermediates, just as expected for such an exothermic reaction. Why is there only one pathway for the Ni case, but three for the Zn? Since Zn(II) is surely a much better Lewis acid than a neutral Ni atom, it is understandable why the Lewis acid−Lewis base adduct does not form in the Ni case. The oxidative cleavage reaction does not occur, because Ni(0) is of course not a strong oxidizing agent. Thus, at least for ^{1}D Ni, the oxidative addition reaction with phosgene is the only pathway available. If ground state ^{3}F Ni is promoted thermally to ^{1}D Ni, made possible by its low excitation energy, then it is possible the reaction with Ni may proceed as we have outlined.

Why is this oxidative addition reaction so exothermic for Ni, while the analogous reaction for Zn^{2+} is less so? This is easily understood again via the VB view of oxidation states[20] in terms of the open shell nature of the Ni atom compared to the closed shell nature of the Zn ion. ^{1}D Ni has open shell electrons that can easily form Ni−Cl bonds, whereas ^{1}S Zn^{2+} does not, as described above. An alternative, more conventionally inorganic explanation is to recognize that, formally, this oxidative addition reaction involves Zn(II) going to Zn(IV) versus Ni(0) going to Ni(II), the latter of which is clearly more favorable. We prefer the insight provided from the VB view of oxidation states, which does not rely on the memorization of relative stabilities of various formal oxidation states.

Implications. Since none of the reactions found have barriers, then the Zn^{2+} and Ni reactions with phosgene are expected to

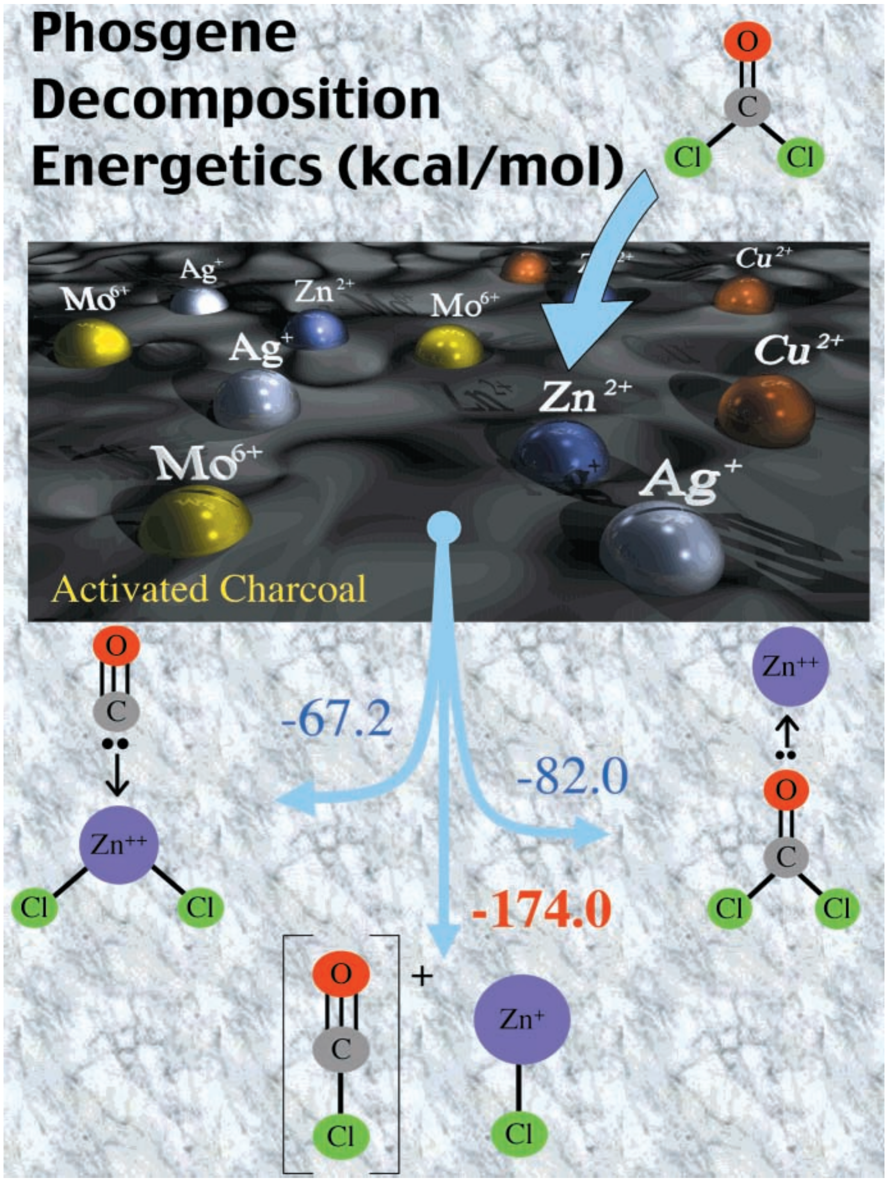

Figure 1. Reaction Paths and MRSDCI Energetics for Phosgene Decomposition by Zn^{2+}.

be gas phase diffusion-controlled rather than reaction-rate-limited. The large exothermicities predicted for these reactions clarifies why Zn^{2+} is a good stoichiometric dopant and why the charcoal filters saturate more quickly relative to agents adsorbed via physical adsorption (such as nerve agents). In the Zn^{2+} case, it is likely that *two* Zn^{2+} ions are saturated for each phosgene molecule (rendering it a less efficient protective agent). This may be a general phenomenon for all the high oxidation state TM ion dopants. Namely, the oxidative cleavage of C−Cl bonds (via transfer of Cl-) by ions in both phosgene and cyanogen chloride may be a general, highly exothermic *stoichiometric* first step. Interestingly, ZnS nanocrystallites recently were used to photoreductively dechlorinate chlorinated aromatics[22] and a Pd-Zn catalyst in acidic solution has been used to dechlorinate polychlorobiphenyls,[23] suggesting that Zn(II) is capable of dechlorination reactions.

By contrast the neutral TM Ni *inserts* into both C−Cl bonds. Though Ni might be an improvement over Zn ions since only one Ni atom reacts per phosgene molecule, it is probably too difficult to keep Ni from oxidizing under ambient conditions and thus it is probably not a practical dopant. (Note that Ni would probably not be present as Ni metal particles, because of the presence of oxygen in the air.) In any case, Ni is still not the ideal case as the reaction is again too exothermic, and hence noncatalytic. Generally, neutral metals are likely to be oxidized under ambient conditions, while high oxidation state metals may be ineffective catalysts because the oxidative cleavage reaction is simply too favorable. Namely, the reaction is so exothermic it is impossible subsequently to get the heteroatoms off the TMs, and hence the filters get saturated. One should look to intermediate oxidation state TMs so as to make the reactions catalytic at ambient temperatures. One possibility would be to explore the use of low oxidation states of cobalt, such as Co(I) up to Co(III), which are present in various states of Vitamin B_{12} (cobalamin). Vitamin B_{12} has been used as a catalyst in the dechlorination of chlorinated hydrocarbons,[24−27] and thus it, or other cobalt complexes[28] or salts, might work as catalysts for the destruction of phosgene.

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