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Registry No. W(CO)₆, 14040-11-0; W(CO)₅, 30395-19-8; bpy, 366-18-7; CO, 630-08-0; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 1-pentene, 109-67-1.

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Mechanism for Chelated Sulfate Formation from SO₂ and Bis(triphenylphosphine)platinum

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Structure and energy surface calculations using the atom superposition and electron delocalization molecular orbital theory show that the first step in the reaction between SO₂ and the dioxygen complex (PPh₃)₂PtO₂ is the coordination of SO₂ with one oxygen atom of the complex, followed by metal-oxygen bond breaking and reorientation, leading to a five-membered cyclic structure. This then rearranges to form the bidentate coordinated sulfate. Alternative pathways are considered and are found to be less favorable.

Introduction

Dioxygen transition-metal complexes have received considerable attention in the past several years because of their important role in biological processes and in catalysis. Several extensive reviews have appeared in the literature summing up the available information on a variety of these complexes.¹ The reactivities of the η²-dioxygen ligand in low-oxidation-state transition-metal complexes have also been investigated in recent years,² particularly their reactions with carbonyl compounds,³ carbon dioxide,⁴ sulfur dioxide,⁵ and olefins.⁶ In most of these reactions the coordinated dioxygen behaves as a nucleophile. Ugo et al. have studied the kinetics of the addition of ketones to (PPh₃)₂PtO₂, forming a pseudo-ozonide.⁷ They found the major pathway to be first order in complex and ketone. This mechanism was thought to involve coordination of the ketone to an axial site of the square-planar complex, followed by intramolecular nucleophilic attack on the carbonyl by dioxygen. Thus they postulated a S_N2-type transition state for this reaction. Collman et al.⁵ have shown from isotopic labeling studies and IR spectroscopy that the coordinated sulfate formed by the reaction between SO₂ and the dioxygen complex of iridium gives an identical isotopic substitution pattern for the two external oxygens, irrespective of whether they start with doubly labeled O₂ or doubly labeled SO₂. They explained this result by postulating the formation of a peroxysulfite intermediate, which is analogous to the pseudo-ozonide in the case of ketones. The

postulated structure of this intermediate is, however, not identical in ref 5a and 5b. In the former, one oxygen atom of SO₂ is attached to the central metal atom, forming a five-membered cyclic structure, whereas in the latter, the sulfur atom from SO₂ bonds to the metal atom, forming a four-membered ring. However, in both cases the O-O bond originating from the dioxygen ligand remains intact. It is the metal-oxygen bond that breaks in the primary step of SO₂ attack on the complex.

There has been no theoretical investigation on the mechanistic details of the steps involved in the ultimate formation of coordinated sulfate. The purpose of this paper is to calculate structures and relative stabilities for the various species possibly involved in the formation of coordinated sulfate by the reaction between SO₂ and the square-planar dioxygen complex of platinum and thus devise a reaction path for this process. We use the atom superposition and electron delocalization molecular orbital (ASED-MO) technique, which has been successfully applied to related problems, including sulfate formation mechanisms in the absence as well as in the presence of transition-metal centers,^{8a-c} and to structure determinations of transition-metal coordination compounds.^{8d,e} The emphasis of this work is on the molecular orbital theory of the bonding. The interaction energies calculated in this work are approximate and depend on the atomic parameter choices. Within this parameter choice, the relative interaction energies for the structures studied are expected to be in the correct order. Our orbital analyses support this expectation by explaining the bonding in terms of molecular orbital symmetry and overlap considerations, which are not qualitatively sensitive to parameter uncertainty. Theory parameters are in Table I. These parameters include ionization potentials whose spacings are based on experimental sources and therefore include the relativistic shifts that occur for platinum.

Results and Discussion

We used peroxobis(phosphine)platinum, (PH₃)₂PtO₂, as a simplified model for the known compound peroxobis(triphenylphosphine)platinum, (PPh₃)₂PtO₂, for all calculations. The O-O bond length of coordinated dioxygen was fixed at the experimental value of 1.51 Å and determined by X-ray measurements,⁹ and the rest of the structure was completely optimized, with bond

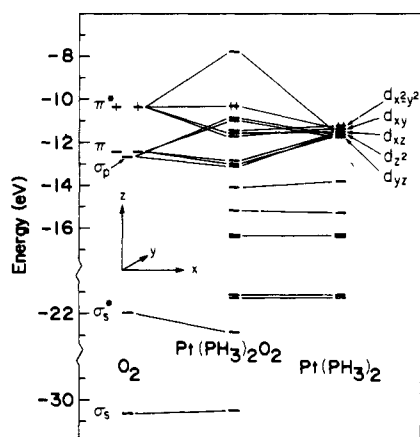
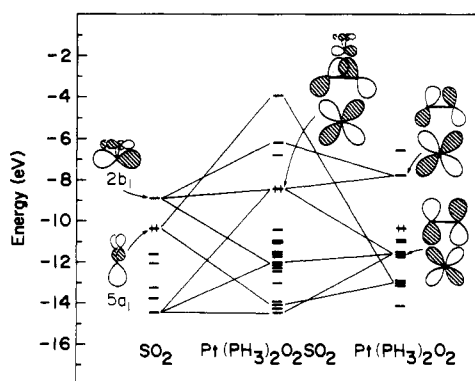
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Table I. Atom Parameters Used in the Calculations:^a Principal Quantum Number (*n*), Ionization Potential (IP) in eV, Slater Exponents (ζ), and Respective Coefficients (*c*) for Double- ζ d Functions

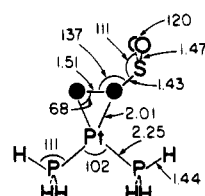
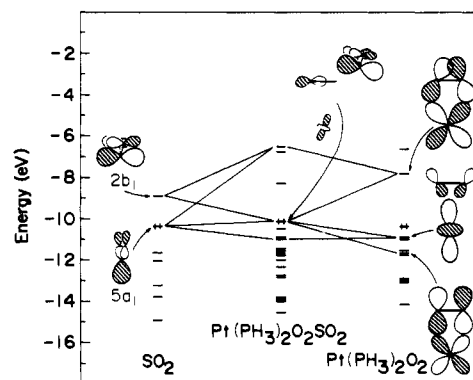
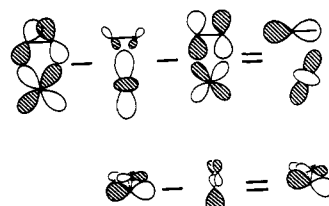
	s			p			d					
	<i>n</i>	IP	ζ	<i>n</i>	IP	ζ	<i>n</i>	IP	ζ_1	c_1	ζ_2	c_2
Pt	6	11.00	2.55	6	6.96	2.25	5	11.60	6.013	0.6562	2.396	0.5711
S	3	22.20	2.22	3	12.36	1.927	3	6.00	1.90			
O	2	26.48	2.046	2	11.62	2.027	3	1.00	2.00			
P	3	18.15	1.881	3	12.49	1.629						
H	1	12.60	1.20									

^aSymbols are as follows: *n*, principal quantum number; IP, ionization potential in eV; ζ and *c*, Slater exponents and their respective coefficients for double- ζ d functions. Ionization potentials are taken from: Lotz, W. *J. Opt. Soc. Am.* **1970**, *60*, 206. Slater exponents are taken from: Clementi, E.; Raimondi, D. L. *J. Chem. Phys.* **1963**, *38*, 2686. Basch, H.; Gray, H. B. *Theor. Chim. Acta* **1966**, *4*, 367. To mimic self-consistency, ionization potentials of Pt, P, and S are increased by 2 eV and those for O and H are decreased by 2 and 1 eV, respectively; ζ is decreased by 0.2 au for O and increased by 0.1 au for S. The numbers in the table include these changes.

**Figure 1.** Molecular orbital correlation diagram for O₂ coordinated to Pt(PH₃)₂ in the η² orientation (O₂ lies in the x-z plane and is parallel to the x axis).**Figure 2.** Diagram as in Figure 1 for SO₂ making a symmetric approach toward O₂ in the Pt(PH₃)₂O₂ complex.

lengths in 0.01-Å increments and bond angles in 1° increments. The O-O bond length was fixed because of excessive stretching from overestimated back-bonding into the π* orbitals. Once the geometric approach of SO₂ was determined, this model restriction was relaxed. The calculated Pt-P distance and P-Pt-P angle are 2.25 Å and 102°, respectively, compared to the experimental values of 2.23 Å and 101.2°. The calculated binding energy of O₂ with Pt(PH₃)₂ is 0.8 eV. The molecular orbital correlation diagram for O₂ coordinating to Pt(PH₃)₂ is shown in Figure 1. The overall binding scheme is qualitatively similar to those found in past CNDO¹⁰ and Xα-SW¹¹ studies of this dioxygen complex.

In our study of sulfate formation the first path considered (after the Pt-O(SO)) interaction was found to be repulsive) was a direct attack by SO₂ on the O-O bond of the dioxygen complex, keeping the SO₂ plane perpendicular to the PtO₂ plane. No binding was

**Figure 3.** Optimized structure when SO₂ attacks one oxygen atom of the dioxygen complex. All HPH angles are assumed to be the same, and the O₂ bond length is fixed (see text). Units are angstroms and degrees.**Figure 4.** Diagram as in Figure 2 for SO₂ making an unsymmetric approach toward O₂ in the Pt(PH₃)₂O₂ complex.**Figure 5.** Linear combinations responsible for the hybridization of the highest occupied molecular orbital shown in Figure 4.

calculated for this mode of approach either, because the net interaction is closed shell as illustrated in Figure 2. The 5a₁ orbital of SO₂ overlaps strongly with the occupied O₂ π_z orbital of the complex, and the antibonding orbital rises rapidly. It is able to donate its electrons to the 2b₁ orbital of SO₂, resulting in a small net charge transfer of 0.3 to SO₂. However, this orbital is the antibonding member of the pair of orbitals formed from the interaction with an occupied O₂ π_z* + Pt orbital of the complex. Some stabilization of this orbital is provided by a higher lying O₂ π_z* - Pt antibonding orbital of the complex, but it is too weak to allow binding of SO₂.

The second pathway considered in detail by us for the reaction between SO₂ and dioxygen in the complex is an electrophilic attack of SO₂ on an oxygen atom lone pair. When SO₂ approaches dioxygen from a side, we find considerable binding between the two. The optimized structure is shown in Figure 3. A similar O₂-SO₂ adduct plays a role in sulfate formation on the surface

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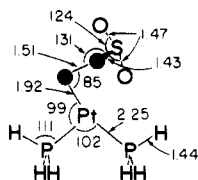


Figure 6. Structure of the transition state for Pt-O bond scission. Note the simultaneous rotation of SO₂. See Figure 3.

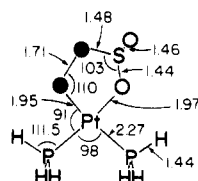


Figure 7. Structure of the postulated five-membered ring intermediate. The O₂ bond length was optimized. See Figure 3.

of NaCl.^{8a,b} The calculated binding energy is 1.5 eV. In this orientation the 2b₁ and 5a₁ orbitals of SO₂ hybridize together when forming bonding molecular orbitals with the dioxygen. Similarly, the complex d_{xy} - π* antibonding, d_{z²} - π antibonding, and d_{xy} + π* bonding orbitals hybridize together. The result is a stabilization of over 1.5 eV for the highest occupied molecular orbital, as may be seen in Figure 4. The specific cause of the stabilization is the removal of the Pt-O₂ antibonding overlap in this orbital. This may be understood by examining Figure 5. The greater participation of the 2b₁ orbital in the highest occupied molecular orbital contributes to a net charge of -1.1 on SO₂. After the formation of this adduct the Pt-O bond that is nearer to SO₂ and the O-O bond are weakened, as indicated by a decrease in their bond orders from 0.21 and 0.52, respectively, in the dioxygen complex to 0.15 and 0.39 in the adduct. The bond order for the second Pt-O bond, which is away from SO₂, increases from 0.21 to 0.28, showing strengthening of this bond. The adduct formation will, therefore, facilitate breaking of the Pt-O bond near the coordinated SO₂. We have carried out calculations on the energy surface for the simultaneous breaking of this Pt-O bond and rotation of the SO₂ plane relative to the Pt-O-O plane (see Figure 3) clockwise. This was done by increasing the Pt-O-O angle in steps of 5°, and for each angle, all other variables, except O-O bond length, were completely optimized. The transition state for Pt-O bond activation is shown in Figure 6. The calculated activation barrier is 0.4 eV if the O-O bond length is fixed at 1.51 Å, the value observed for the dioxygen complex, and is only 0.1 eV if the O-O bond length is fixed at the value calculated for the five-membered ring (Figure 7). The actual value of the barrier should be small. This estimate of the activation barrier is somewhat lower than the value of the activation enthalpy for nucleophilic substitutions involving a platinum(II) complex¹² quoted by Ugo et al.⁷ (10-20 kcal/mol). After the transition state the Pt-O angle continuously increases and the dihedral angle between the planes Pt-O-O and SO₂ continuously decreases with a lowering of energy until one oxygen atom originally belonging to SO₂ forms a bond with platinum, thus forming a five-membered ring structure. Figure 7 shows the optimized structure of this ring system. This ring structure is similar to the pseudo-ozonide structure, which has been well characterized as a result of the reaction between ketones and dioxygen complexes. The binding energy of SO₂ with the dioxygen complex to form this ring structure is 2.6 eV. After the formation of this intermediate ring structure, the O-O bond originating from the dioxygen ligand should break in order to form coordinated sulfate. We find from our calculations that when the SO plane in the five-membered ring is rotated relative to the OPt plane, the O-O bond breaks without barrier. For every 5° rotation of the SO plane all the other variables were completely optimized. It is found

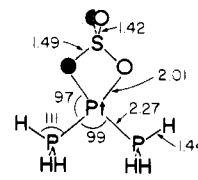


Figure 8. Structure of the chelate product.

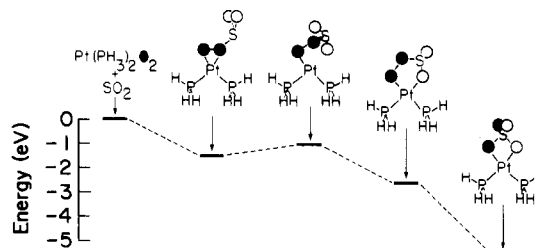


Figure 9. Relative energies of the various species involved in the ultimate formation of coordinated sulfate.

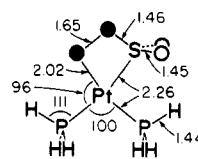


Figure 10. Structure of the four-membered ring discussed in the text.

that, during this continuous rotation, the sulfur atom slowly comes closer to the oxygen atom joined to platinum and originally belonging to the dioxygen ligand, with a continuous decrease of energy until coordinated bidentate sulfate, shown in Figure 8, is formed. The reaction energy of SO₂ and the dioxygen complex to form coordinated sulfate is calculated to be 5.5 eV. These reaction steps and relative energies of various postulated intermediate species involved in the chelated sulfate formation are sketched in Figure 9. The rate-determining step for the overall reaction is, therefore, the breaking of one Pt-O bond of the dioxygen complex with simultaneous rotation and bond formation of one oxygen atom of SO₂ with the platinum atom, forming the five-membered intermediate structure. After this, the reaction is downhill. This pathway also explains the results of isotopic labeling studies of Collman et al.⁵ whereby one oxygen atom originally belonging to the dioxygen ligand moves outside, giving the same isotopic substitution pattern irrespective of the origin of the labeled oxygen.

We have also looked at the possibility of forming a four-membered ring intermediate with a bond between platinum and sulfur, as suggested earlier.^{5b} There are two possible ways this could happen. The first way requires prior formation of an activated form of the dioxygen complex, which may react rapidly with SO₂ to form the four-membered cyclic structure. This is similar to the minor pathway given in ref 7 for the reaction between ketones and the dioxygen complex. The second way may be a concerted breaking of a Pt-O bond and forming of the Pt-S bond when SO₂ approaches the dioxygen complex from the side.^{5b,11b} We tried to bring SO₂ toward one Pt-O bond of the PtO₂ moiety from all possible angles and found there was no binding of SO₂, which suggests the concerted pathway is unlikely. Nevertheless, the first pathway, which requires the formation of an activated complex, possibly by breaking one of the Pt-O bonds under the influence of SO₂ or solvents, followed by the attack of SO₂ to form the four-membered ring, is possible. The optimized structure of this four-membered ring is shown in Figure 10. The calculated binding energy of SO₂ with the dioxygen complex to form this structure is 3.1 eV, showing that the four-membered ring structure is more stable than the five-membered ring structure. Considering the nature of the ultimate product of the reaction, we tried breaking the Pt-S bond of this four-membered ring and forming the Pt-O bond by rotation of the SO₂ moiety and found it was a high-energy pathway. The calculated activation barrier

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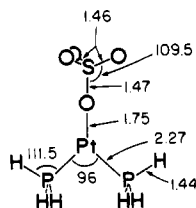


Figure 11. Structure of the product when sulfate is constrained to be monodentate.

on going from a four-membered to a five-membered cyclic structure is 1.9 eV. Our calculations, therefore, suggest that the formation of a four-membered ring is less probable.

Finally, we calculate the structure and stability of monodentate sulfate coordinated to $\text{Pt}(\text{PH}_3)_2$. The calculated structure is shown in Figure 11. The binding energy of SO_2 with the dioxygen complex to form monodentate sulfate is 4.9 eV, showing that it is 0.6 eV less stable than the bidentate sulfate structure, as ex-

pected on the basis of the structure of molecular sodium sulfates.¹³

Conclusions

We have found sulfate formation from sulfur dioxide and bis(phosphine)platinum proceeds most readily through a five-atom cyclic intermediate, which is similar to the stable pseudo-ozonide that forms when ketones react instead of SO_2 . Our finding that the sulfur in SO_2 attacks one end of coordinated O_2 in the initial step suggests the ketone may do the same, rather than first coordinating to an axial Pt site as was suggested.⁷ The four-atom cyclic intermediate is eliminated on the grounds that if it does form it transforms to sulfate only with difficulty and its formation is hindered by the necessity of activating the coordinated O_2 ligand.

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Generalized Molecular Orbital Calculations on Transition-Metal Dioxygen Complexes: Model for Manganese Porphyrin

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Restricted Hartree-Fock plus configuration interaction and generalized molecular orbital plus configuration interaction calculations are reported for several structural models of the dioxygen complexes of manganese(II) porphyrins. An analysis of the results suggests a ground-state structure with a side-on (Griffith) dioxygen and oxygen atoms eclipsing the ring nitrogens. The calculation predicts three singly occupied metal orbitals ($t_2^2e^1$ in pseudocubic symmetry; $\sigma^1\pi^1\delta^1$ in pseudolinear symmetry) in agreement with the ESR results. In contrast to previous ab initio calculations, the CI results also predict a ground-state end-on (Pauling) structure with three unpaired electrons in metal orbitals that would be consistent with the ESR. On the basis of our calculations alone, this structure could not be eliminated as a possibility.

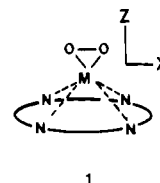
Introduction

At low temperature the reversible reaction of molecular oxygen with a manganese porphyrin yields a pentacoordinate complex, $\text{Mn}(\text{O}_2)\text{P}$ (P = porphyrin dianion).¹ The deoxygenated manganese porphyrin exists as a high-spin d^5 Mn(II) complex, with a single electron in each of the 3d orbitals. These manganese porphyrins contain a single axial ligand,² which is replaced by the O_2 ligand in the manganese-dioxygen porphyrin. Electron paramagnetic resonance (EPR) studies of $\text{Mn}(\text{O}_2)\text{P}$ indicate the presence of three unpaired electrons, and ^{17}O substitution shows that little unpaired spin density resides on the O_2 ligand.¹

Other manganese complexes that also form dioxygen adducts have as other ligands phthalocyanine,³⁻⁶ catechol,⁷ salen,⁸ sorbitol,⁹

tertiary phosphines,¹⁰ and carbonyls.¹¹ These complexes normally contain one O_2 ligand per Mn atom, although the monomeric $\text{Mn}(\text{O}_2)\text{Pc}$ (Pc = phthalocyanine) compound is an intermediate in the formation of the μ -oxo dimer.^{3,4} Coleman and Taylor have recently reviewed reactivity-structure correlations in these complexes, and Gubelmann and Williams have reviewed both these and related complexes.¹²

Although no crystal structure has been obtained for the manganese dioxygen porphyrin, the ESR and particularly the IR ($^{16}\text{O}_2$, $^{18}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$) results^{1d} seem best interpreted as a side-on or Griffith geometry (1). Formally this would correspond to a peroxo



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complex, $\text{Mn}^{4+}\text{O}_2^{2-}$. Three reasonably low-energy electronic configurations $[(x^2 - y^2)^1(xz)^1(yz)^1]$, $[(x^2 - y^2)^1(yz)^1(z^2)^1]$, and $[(x^2 - y^2)^1(yz)^1(xy)^1]$ were proposed to provide acceptable solutions to the ESR results. Extended Hückel calculations were reported to favor the $[(x^2 - y^2)^1(yz)^1(z^2)^1]$ configuration.¹³ However, the

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