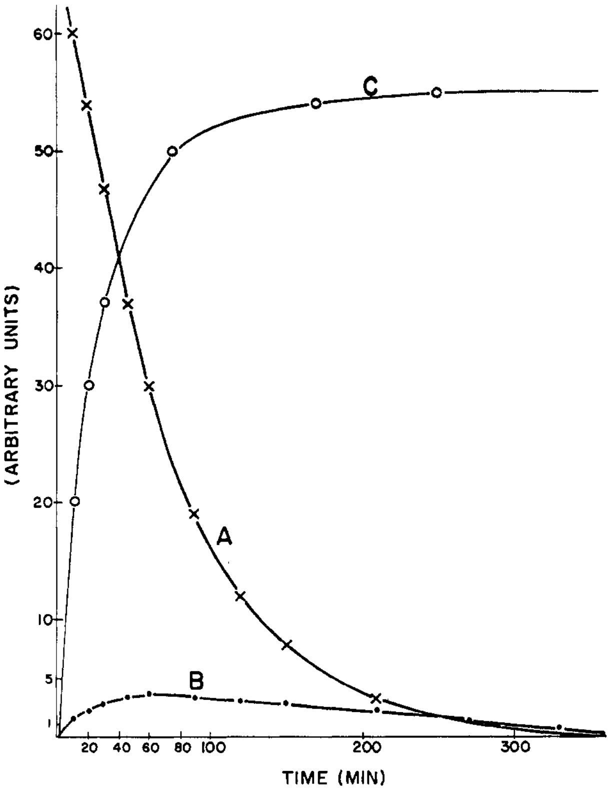

Figure 3.—Concentration change with time of $Ni^{III}TPP^+$ (A), $Ni^{II}TPP^+$ (B), and $Ni^{II}TPP$ (C); A and B measured by epr; C, by optical spectroscopy.

signal was measured directly from the experimental spectrum. Table I summarizes the epr data of the two Ni compounds and that of the nonmetallic oxidation product, $H_2TPP \cdot {}^+$.[12] Figure 2 gives the variation of the two signals with time. The intensity variation with time of the two epr signals and the optical intensity recovery (~96%) of the Soret band (418 mμ) peak height of the $Ni^{II}TPP$ complex indicate a consecutive reaction mechanism (Figure 3), with a rate constants ratio of about 10.

Discussion

The two epr signals are sufficiently distinct to assign the first one to a square-planar d^7 configuration,[17] compatible with $Ni^{III}TPP^+$ cation, and the second one to a free-radical ion, $Ni^{II}TPP \cdot {}^+$, in which the unpaired electron is associated with the ligand π system. The oxidized nonmetallic ligand has different g values. These epr results combined with trends we found for oxidation behavior in the series iron–zinc TPP[12] suggest that the first oxidation produces the $Ni^{III}TPP^+$ cation. The second oxidation product is apparently $Ni^{III}TPP^{2+}$ rather than $Ni^{IV}TPP^{2+}$.[12] This species, which we see by cyclic voltammetry, is unstable and rapidly returns to the $Ni^{III}TPP^+$ cation *via* an electron capture. This oxidation mechanism is consistent both with the epr result that only one signal is produced after oxidation at various potentials and with the observation that the area under the reduction peak in the cyclic voltammogram is more than half of the area of the oxidation peak (Figure 1). This type of cyclic voltammogram precludes the possibility of having one-step two-electron transfer. The optical spectrum of the two-electron oxidized species could not be obtained without interference from the decomposition products, which in turn could not be observed at all under our experimental conditions (see Figure 1 of ref 12). The $Ni^{III}TPP^+$ cation, which is the monooxidation product, slowly decomposes to the original $Ni^{II}TPP$ complex by way of the cation radical $Ni^{II}TPP \cdot {}^+$ (Figure 3). The decomposition mechanism of $Ni^{III}TPP^+$ to the free-radical cation $Ni^{II}TPP \cdot {}^+$ is uncertain. The overall reaction is a ligand-to-metal atom electron transfer; however, at the present time we do not have enough data to determine the detailed mechanism.

However, regardless of the exact decomposition mechanism and despite the strong covalency in metalloporphyrins by observing the two different epr signals, we could distinguish between the metal and the ligand oxidation products of the $Ni^{II}TPP$ complex. Therefore, we believe that in this case we have actually identified a planar Ni(III) complex with a $3d^7$ configuration,[17] as opposed to assigning a formal oxidation state of 3 with an undetermined configuration.

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(17) The term square planar is used in the same meaning as in ref 7. Generally speaking, in solution the metalloporphyrins (particularly the cationic species) can form bonds with ligands in their fifth and sixth coordination positions. However, even under these conditions the main features of the square-planar unit are preserved.

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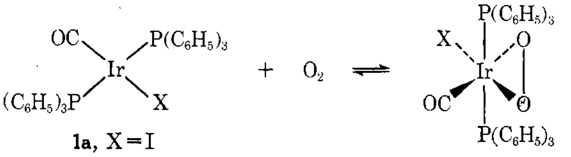
An Oxygen-18 Study of the Reaction between Iridium- and Platinum-Oxygen Complexes and Sulfur Dioxide to Form Coordinated Sulfate

BY R. W. HORN,[1] E. WEISSBERGER, AND J. P. COLLMAN[2]

Received March 20, 1970

In 1963, the remarkable iridium(I) complex **1** was found to form reversibly a 1:1 complex with O_2.[3] In the intervening years, diamagnetic mononuclear oxy-



1a, X = I
b, X = Cl

2

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[1] National Science Foundation predoctoral fellow.

[2] Queries should be sent to this author.

[3] L. Vaska, *Science*, **140**, 809 (1963).

gen complexes of Fe,[4] Ru,[5] Rh,[6] Ir,[7] Ni,[8] Pd,[8a,d,9a,b,c] and Pt[8a,d,e,9] have been formed by this conceptual oxidative addition. All diamagnetic mononuclear O_2 complexes thus far studied by X-ray diffraction consist of triangular structures in which the two oxygen atoms are equivalently bound to the metal.[7a,8e] The O–O bond lengths in these complexes vary over a wide range, from 1.31 to 1.66 Å, depending on the electron density at the central metal, which is strongly influenced by the other ligands.[7a] Irreversibly bound O_2 is characterized by longer O–O bond lengths.[7a,10]

Such oxygen complexes exhibit an infrared band between 800 and 900 cm^{-1}.[8c,d] Isotopic substitution of O_2 shifts this band by an amount calculated for a simple harmonic oscillator. Examples are shown in Table I. That this absorption is not caused by a simple O–O stretching mode is indicated by the insensitivity of this frequency to the O–O bond length. Additional bands between 490 and 633 cm^{-1} are also shifted by isotopic substitution but not by the calculated amount (Table I). These frequencies are more strongly dependent on the nature of the metal and the accompanying ligands and probably involve some degree of metal–oxygen vibration.

Coordinated molecular oxygen is kinetically more reactive than the free paramagnetic molecule.[11] Phosphines,[8a,9a,c] isocyanides,[8b,d] CO,[11] NO,[11] NO_2,[11,12] and SO_2[11–13] have been oxidized with oxygen complexes. Both catalytic[8a,9a] and stoichiometric[11–13] reactions have been reported. The stoichiometric reaction of SO_2 with coordinated O_2 to form coordinated sulfate seems to be a reaction characteristic of all such oxygen complexes. In several instances free O_2 also reacts with metal–SO_2 complexes, but this process does not always take place.

We have begun to study the mechanisms by which metal–O_2 complexes react with the above reductants in the hope of developing a clearer understanding of biological and industrial catalytic oxygenation. The present paper reports a study of the reaction between metal–O_2 complexes and SO_2 by employing ^{18}O isotopic substitution and infrared spectroscopy.

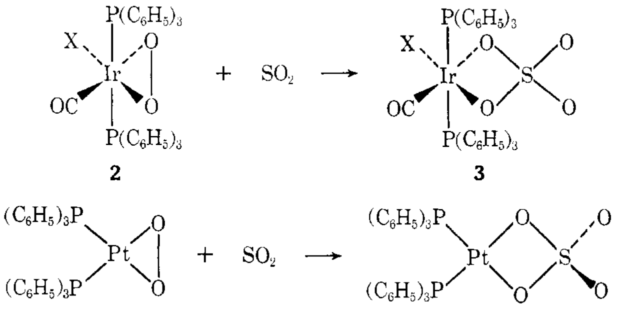
TABLE I

INFRARED ABSORPTIONS INVOLVING OXYGEN MOTION

Compound	800–900-cm^{-1} region[a] $^{16}O_2$	$^{16}O^{18}O$	$^{18}O_2$	480–603-cm^{-1} region Normal	Enriched	Ref
$Ir(P(C_6H_5)_3)_2COCl(O_2)$	858	834 (833)	810 (808)	633	610	*c*
	856	832	809			*d*
	858					*e*
	860					*f*
$Ir(P(C_6H_5)_3)_2COBr(O_2)$	860	835 (835)	811 (811)	629	608	*c*
	862					*e*
$Ir(P(C_6H_5)_3)_2COI(O_2)$	862	837 (837)	813 (812)	625	595	*c*
	862					*e*
$Ir(P(C_6H_5)_3)_2Cl(O_2)$	852	828 (827)	804 (803)	563	. . .	*i*
$[Ir(diphos)_2(O_2)]Cl$[b]	843	818 (818)	793 (794)	547	516	*c*
	845					*g*
$Ni(t\text{-}C_4H_9NC)_2(O_2)$	898	873 (871)	848 (846)	549	540	*d*
$Pd(t\text{-}C_4H_9NC)_2(O_2)$	893	868 (866)	837 (841)	490	484	*d*
$Pd(P(C_6H_5)_3)_2(O_2)$	875					*d*
$Pt(P(C_6H_5)_3)_2(O_2)$	822	801 (799)	777 (775)	. . .	. . .	*c*
	830					*d*
	813					*h*

[a] Values in parentheses are calculated assuming a simple diatomic oscillator. [b] diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. [c] This work. [d] Reference 8d. [e] Reference 10a. [f] Reference 3. [g] Reference 7a. [h] Reference 9a. [i] D. Valentine, J. Valentine, and J. P. Collman, unpublished results.

Reactions of iridium– and platinum–oxygen complexes **2** and **4** with SO_2 to form the sulfato complexes **3** and **5** have been examined.



2 **3**

4 **5**

Labeled oxygen complexes were prepared from nonstatistically labeled oxygen under reversible and irreversible conditions (Table II). Iodoperoxycarbonylbis(triphenylphosphine)iridium **2a** was formed irreversibly[10] in $CHCl_3$ from statistically and nonstatistically enriched O_2. The chloro analog **2b** was prepared under reversible[10] conditions in chlorobenzene using nonstatistically enriched O_2. The distribution of oxygen isotopes in the oxygen complexes was calculated from the infrared spectra. The experimental data in Table II show that the initial isotopic distribution is maintained in the product complexes. This result proves that oxygen atom scrambling does not take place during the reversible formation of the chloro–oxygen complex.

In order to use isotopic shifts for studying the mechanism of the SO_2 oxidation, it is necessary to assign the infrared-active bands arising from coordinated sulfate. Free sulfate, monodentate sulfate,

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TABLE II

OXYGEN ISOTOPE DISTRIBUTION (%)

Compound	Overall ^{18}O	Statistical $^{16}O_2$	Statistical $^{16}O^{18}O$	Statistical $^{18}O_2$	Reagent O_2 $^{16}O_2$	Reagent O_2 $^{16}O^{18}O$	Reagent O_2 $^{18}O_2$	Product $^{16}O_2$	Product $^{16}O^{18}O$	Product $^{18}O_2$
$Ir(P(C_6H_5)_3)_2COI(O_2)$	91	0.8	16.4	82.8	0.8	16.4	8.28	1.0	16	82
$Ir(P(C_6H_5)_3)_2COI(O_2)$	50.2	24.8	50.0	25.2	45.3	9.0	45.7	49	12	38
$Ir(P(C_6H_5)_3)_2COCl(O_2)$[a]	48.2	26.9	49.9	23.2	47.6	8.7	43.8	53	7.0	40

[a] Reversibly formed in C_6H_5Cl; $T = 75°$, $P_{O_2} = 0.35$ atm, time = 18 hr.

TABLE III

CORRELATION TABLE FOR T_d, C_{3v}, AND C_{2v}

Point group	ν_1	ν_2	ν_3	ν_4
T_d	A_1(R)[a]	E(R)	T_2(I,R)	T_2(I,R)
C_{3v}	A_1(I,R)[b]	E(I,R)	A_1(I,R) + E(I,R)	A_1(I,R) + E(I,R)
C_{2v}	A_1(I,R)	A_1(I,R) + A_2(R)	A_1(I,R) + B_1(I,R) + B_2(I,R)	A_1(I,R) + B_1(I,R) + B_2(I,R)

[a] R indicates a Raman-active mode. [b] I indicates an infrared-active mode.

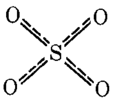
TABLE IV

IR ABSORPTIONS (CM^{-1}) OF VARIOUS SULFATE COMPOUNDS

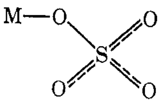
Compound		ν_3		ν_1	ν_4	ν_2	Ref
Free SO_4^{2-}		1140		983 (R)	613	454 (R)	e
$[Co(NH_3)_5SO_4]Br$		1143–1117	1044–1032	970	645, 604	438	e
$[Co(en)_2SO_4H_2O]Br$		1130	1070	978	645, 625	a	f
$[Co(en)_2SO_4]Br$	1211	1176	1075	993	647, 632	515	f
$Pd(NH_3)_2SO_4 \cdot H_2O$		1140–1100	1050–1030	996	a	a	g
$Pd(C_6H_5)SO_4$	1240	1125	1040–1015	955	a	a	g
$Pd(py)_2SO_4 \cdot H_2O$	1235	1125	1020	930	a	a	g
$(CH_3)_2SO_4$	1400	1200	875	752	a	a	h
$Pt(P(C_6H_5)_3)_2SO_4$	1279	1165, 1150		880, 871	650[d]	a	i
$Pt(P(C_6H_5)_3)_2SO_4$	1281	1168, 1154 (1155)[c]		882, 871 (879)[c]	659, 609	b	j
$Pd(P(C_6H_5)_3)_2SO_4$	1265	1155	1110[e]	920	a	a	k
$Pd(P(C_6H_5)_3)_2SO_4$	1262	1148		896	645, 609	b	j
$Ir(P(C_6H_5)_3)_2COI(SO_4)$	1296	1172	880	856	662, 610	549[e]	j
$Ru(P(C_6H_5)_3)_2(NO)Cl(SO_4)$	1300	1170	885	860		a	l

[a] Frequencies in this range were not reported. [b] Frequencies in this range were not observed. [c] Doublet collapsed to this frequency in solution. [d] Our assignment. [e] K. Nakamoto, J. Fujita, S. Tamaka, and M. Kobayaski, *J. Amer. Chem. Soc.*, **79**, 4904 (1957). [f] C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 1993 (1961). [g] Reference 7a. [h] S. Detoni and D. Hadzi, *Spectrochim. Acta, Suppl.*, 11, 601 (1957). [i] Reference 12. [j] This work. [k] R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Commun.*, 1498 (1968). [l] W. R. Roper, private communication.

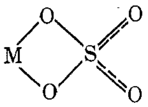
bidentate sulfate, and bridging sulfate belong to the T_d, C_{3v}, C_{2v}, and C_{2v} point groups, respectively.



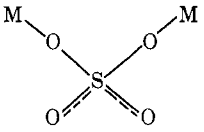
Td



C_{3v}



C_{2v}



C_{2v}

The bands allowed by infrared and Raman selection rules for these symmetries are illustrated in Table III. Infrared data for a series of sulfate complexes taken from the literature and the present work are presented in Table IV. The different types of coordinated sulfate can usually be distinguished by the fact that the ν_3 and ν_4 modes each give rise to two ir bands in the monodentate and three in the bidentate form. This point is illustrated by comparing the ir bands assigned to $[Co(NH_3)_5SO_4]Br$ and $[Co(en)_2SO_4]Br$. The ir bands assigned to the sulfate in $IrI(SO_4)(CO)(P(C_6H_5)_3)_2$ on the basis of isotopic shifts are consistent with a bidentate sulfate. The presence of four bands in the 1300–850-cm^{-1} region are assigned to the three ν_3 and the single ν_1 bands expected for pseudo C_{2v} symmetry. The similarity between the spectrum of this iridium(III) sulfate and $RuCl(SO_4)(NO)(P(C_6H_5)_3)_2$ described by Roper as a bidentate sulfate is apparent. Our supposition that the iridium(III) sulfate is bidentate and thus coordinatively saturated is supported by its failure to coordinate with additional CO.

The low frequencies (880 and 885 cm^{-1}) measured for the lowest ν_3 bands in the d^6 iridium(III) and ruthenium(II) sulfates surprised us. These values are similar to the 875-cm^{-1} absorption tentatively assigned to this absorption in dimethyl sulfate, but this frequency is much lower that that (1075 cm^{-1}) reported for the bidentate cobalt(III) sulfates shown in Table IV. On the other hand, the ν_1 frequency is also much higher in the cobalt(III) sulfate. Tentatively, we suggest that these frequency differences are caused by variations in the degree of covalent bonding. Using the more soluble $IrI(SO_4)(CO)(p\text{-}CH_3C_6H_4P(C_6H_5)_2)_2$ the sulfate absorption bands were found to be the same whether measured in $CHCl_3$ solution, or in a KBr disc, ruling out solid-state effects.

On the basis of the ir bands we have been able to assign to coordinated sulfate in $Pd(SO_4)(P(C_6H_5)_3)_2$ and $Pt(SO_4)(P(C_6H_5)_3)_2$, there is some uncertainty about the bidentate nature of sulfate in these complexes. One of the ν_3 absorptions expected from C_{2v} symmetry in a bidentate sulfate is missing. The band at 1110 cm^{-1} assigned to sulfate in the palladium complex by Cariati[14] was also observed by us, but as a weak band which did not shift upon ^{18}O substitution. A logical contaminant, $(C_6H_5)_3PO$, absorbs strongly at this frequency. Three-coordinate platinum(II) or palladium(II) complexes seem unlikely, and we hesitate to assign a monodentate structure to these sulfate complexes because of the apparent absence of an absorption band. Nevertheless, this dilemma cannot be resolved unequivocably without an X-ray diffraction study.

The reactions with the iridium– and platinum–oxygen complexes were carried out under a variety of isotopic substitutions. The iodo–iridium complex was chosen in preference to the chloro and bromo analogs (which undergo the same reaction) because of the greater stability of the iodo–oxygen complex. Table V summarizes the bands assigned to oxygen-dependent vibrations with those of normal ^{16}O content shown in the first row of each column.

TABLE V
INFRARED ABSORPTIONS (CM^{-1}) DEPENDENT UPON SULFUR-BOUND OXYGEN[a]

$Ir(P(C_6H_5)_3)_2COI(SO_4)$

1296	1172	880	856	662	610	549
1280	1143	843	822	649	595	543
1257	1126			633		538
						532
						527

$Pt(P(C_6H_5)_3)_2(SO_4)$

1281	1168, 1154	828, 871	659	609
	1155[b]	879[b]		
1262	1135	850, 838	642	597
1242	1120		632	587
			624[c]	

[a] The first line under each compound gives the absorption in the normally enriched material. Subsequent lines give bands appearing with increasing ^{18}O content. [b] Doublet collapsed to this frequency in solution. [c] Uncertain assignment.

Oxidation of the sulfur dioxide was accomplished under a variety of ^{18}O distributions. The two extreme cases are depicted as reactions 1 and 2. Maximum O_2 enrichment was 91%; maximum SO_2 enrichment was 90%.

$$M^{18}O_2 + S^{16}O_2 \longrightarrow MS^{18}O_2{}^{16}O_2 \qquad (1)$$

$$M^{16}O_2 + S^{18}O_2 \longrightarrow MS^{18}O_2{}^{16}O_2 \qquad (2)$$

The highest frequency band in the ir spectrum of the iridium sulfate appears at 1296 cm^{-1} and can be assigned with certainty to the antisymmetric stretch of the two external, uncoordinated oxygen atoms. Upon isotopic substitution of the iridium sulfate, three peaks appear in the upper 1200-cm^{-1} region at 1296, 1280, and 1257 cm^{-1} (Table V). These bands are clearly resolved in the spectrum of the iridium sulfate, but the similar three bands are not well separated in the spectrum of the platinum sulfate. Clearly, the three bands in the upper 1200-cm^{-1} region can be ascribed to the external $^{16}O^{16}O$, $^{16}O^{18}O$, and $^{18}O^{18}O$ isotopic species.

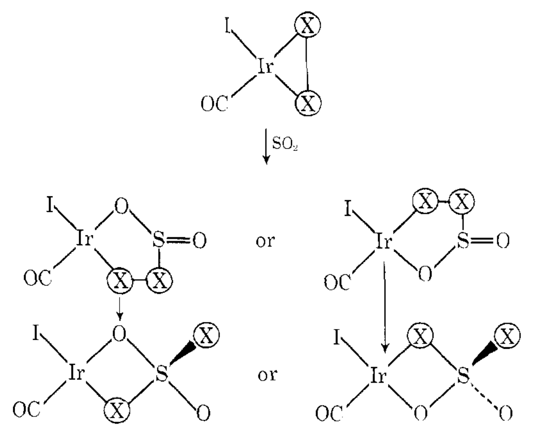


Figure 1.—Mechanism of sulfate formation; only the ligands in the plane containing the MO_2 group are shown.

The iridium sulfates resulting from reactions 1 and 2 have identical spectra in the upper 1200-cm^{-1} region. In neither case do we find the band at 1257 cm^{-1} assigned to two external ^{18}O atoms. This result leads to two conclusions. Intramolecular rearrangement of sulfate has not taken place since this would scramble the oxygen atoms and afford 20.5% of the species containing two external ^{18}O atoms (starting with 90% O_2 or SO_2 statistically labeled with ^{18}O). Metal–oxygen bond cleavage must have taken place during the reaction to account for the identical isotopic substitution pattern observed for the two external oxygens, starting from either doubly labeled O_2 or doubly labeled SO_2.

These results can be accounted for by the mechanism shown in Figure 1. We propose that a peroxysulfite intermediate is formed wherein the two oxygen atoms in the peroxy group are those originating as O_2. The peroxide bond would be expected to break so that one of the peroxy atoms migrates to the external position and the other remains attached to the metal. This mechanism demands that one of the two oxygen atoms in the O_2 molecule as well as one of the oxygen atoms in the SO_2 molecule each assumes an external position.

Differences in the products formed from eq 1 and 2 could arise only in the internal oxygen atoms of the sulfate. Because of the presence of different *trans* groups, CO and I, two isomers with one internal ^{18}O are possible both for the postulated intermediate peroxysulfite and for the product sulfates (Figure 1). Because of the diverse *trans* effects of CO and I, one of the two possible intermediate isomeric peroxysulfites should be more rapidly formed than the other. This would lead to differences in the amount of isotopic isomers distinguished by the position of the internal ^{18}O, depending upon whether the O_2 or the SO_2 was labeled. Such differences are consonant with changes we find in the 850-cm^{-1} region of the spectra of iridium(III) sulfates formed by labeling the O_2, compared with labeling the SO_2 (eq 1 and 2). We are unable to assign these bands to a stretching mode of a specific

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[14] F. Cariati, R. Ugo, and C. Cariello, *Inorg. Chem.*, **5**, 1128 (1968).

oxygen in either isotopic isomer because of the composite nature of the vibrational modes, further lowering of symmetry by introducing isotopes, and the overlap between the lower ν_3 and the ν_1 band upon isotopic substitution.

Relative intensities observed for the antisymmetric external SO_2 stretching bands for the three isotopic species produced in different experiments are compared with values calculated on the basis of the presumed mechanism (Table VI). Intensities were estimated from peak heights. The observed and calculated values are well within the substantial error expected from this crude experiment.

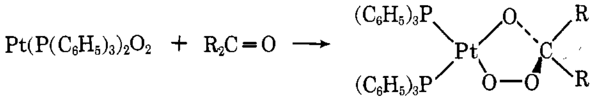
TABLE VI

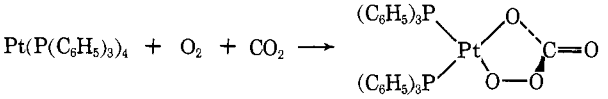
OBSERVED AND CALCULATED ISOTOPIC DISTRIBUTIONS FOR THE 1296-CM^{-1} REGION OF $Ir(P(C_6H_5)_3)_2COI(SO_4)$

Reagent atom % ^{18}O		Overall % ^{18}O	Obsd product distribution,[a] %			Calcd product distribution,[b] %		
O_2	SO_2		$^{16}O_2$	$^{16}O^{18}O$	$^{18}O_2$	$^{16}O_2$	$^{16}O^{18}O$	$^{18}O_2$
91	...	45.5	17	83	...	9	91	...
91	49	70.0	4	51	45	4.6	51	44.4
91	90	90.5	...	20	80	0.2	17.1	82.7
...	49	24.5	52	48	...	51	49	...
...	90	45.0	17	83	...	10	90	...

[a] Peak intensities probably have an accuracy of ±10%. [b] Distributions calculated on the basis of the mechanism shown in Figure 1.

There is precedent for peroxy chelates analogous to the peroxysulfite proposed herein. A pseudo "ozonide" was obtained from reaction of $Pt(P(C_6H_5)_3)_2O_2$ with acetone or acetaldehyde (eq 3).[15] Treatment of the platinum–oxygen complex with CO_2 afforded a peroxycarbonate (eq 4).[16]


(3)


(4)

Ugo[15] has suggested that the ketone group substitutes directly into the O–O bond. On the other hand, if our interpretation of the SO_2 oxidations is generally applicable, the pseudo "ozonide" product of eq 3 and the peroxycarbonate from eq 4 will contain a peroxy function, wherein both oxygen atoms originate as molecular oxygen. We intend to study this prediction using isotopically labeled oxygen.

The reaction between $Pt(P(C_6H_5)_3)_2O_2$ and SO_2 was also studied by isotopic substitution. The peaks in the external SO_2 region were broad and poorly resolved so that it was not possible to measure the relative intensities of the bands at 1280, 1265, and 1242 cm^{-1} assigned to the $S^{16}O^{16}O$, $S^{16}O^{18}O$, and $S^{18}O^{18}O$ groups in the labeled sulfates. However, it is clear that the sulfates prepared from eq 1 and eq 2 have indistinguishable ir spectra. Without better data we are unable to distinguish between intramolecular rearrangement of the labeled sulfate and a mechanism similar to that proposed previously for the iridium case. It should be noted that the two groups *trans* to the oxygen atoms in the platinum sulfate are identical in contrast to the iridium(III) sulfate. The question concerning the bidentate nature of the sulfate further clouds the issue in the instance of the platinum complex.

Experimental Section

Standard literature procedures were used to prepare $IrL_2CO(X)$ (L = $P(C_6H_5)_3$, *p*-$CH_3C_6H_4P(C_6H_5)_2$; X = Cl, Br, I)[10a,11b] and $Pt(P(C_6H_5)_3)_2(C_2H_4)$. $Pd(P(C_6H_5)_3)_2(SO_4)$ was prepared according to Levinson and Robinson.[17] Normally enriched oxygen adducts were prepared by bubbling O_2 through benzene or $CHCl_3$ solutions of the precursor compound. Adducts were precipitated with methanol (Ir adducts) or hexane (Pt adduct). Normal sulfates were prepared by bubbling SO_2 through solutions of the proper oxygen adduct.

Oxygen-18-enriched gases were handled by vacuum techniques. To prepare O_2 adducts, the precursor compound (10–40 μmol) was placed in a flask (10–20 ml) and dissolved in deoxygenated solvent. After four freeze–pump cycles, O_2 was introduced and the sample left until reaction was complete. Platinum adducts formed rapidly, while iridium adducts took from 12 to 24 hr to form at the O_2 pressures used (up to 120 Torr). A threefold excess of O_2 was generally employed. Oxygen adducts were precipitated, filtered, and dried. Care was taken to exclude CO_2 from the platinum preparations. Oxygen-18, enriched O_2, and SO_2 were obtained from Miles Labs, Inc., Elkhart, Ind. Preparations using enriched SO_2 were as follows.

$Pt(P(C_6H_5)_3)_2(O_2)$ + $S^{18}O_2$.—1. Solid oxygen adduct (10 μmol) was placed in a 10-ml flask. 2. Sulfur dioxide (approximately 15 molar excess based on Pt) was frozen into the reaction vessel. 3. The flask was warmed to room temperature. As the solid SO_2 melted, $Pt(P(C_6H_5)_3)_2(O_2)$ reacted, yielding a yellow solution that on evaporation of the SO_2 left a glassy yellow solid. 4. The yellow solid was dissolved in CH_2Cl_2. The slow addition of ether to the solution gave off-white crystals, $Pt(P(C_6H_5)_3)_2(SO_4)$. The infrared spectrum of these crystals was better resolved than that of the glassy material.

$Ir(P(C_6H_5)_3)_2COI(SO_4)$.—Iridium sulfate compounds were prepared in a manner similar to preparation of enriched oxygen adducts. Reaction times ranged from 12 to 24 hr using a threefold excess of $S^{18}O_2$. When necessary, methanol was used as a precipitant, although moderately large red crystals of the sulfate generally formed during the reaction time.

Infrared spectra were obtained using Perkin-Elmer Model 457 and 621 spectrometers. Solid-phase spectra were obtained using KBr disks. Microanalyses were performed by the Microanalytical Laboratory in the Chemistry Department at Stanford University.

Solution spectra of $Pt(P(C_6H_5)_3)_2(SO_4)$ were generally avoided after it was found that the sulfate exchanges with KBr cell windows depositing K_2SO_4. This observation was confirmed by adding solid KBr to a solution of the sulfate in CH_2Cl_2. After 1 hr the solution was filtered and ether was added to the filtrate. Only $Pt(P(C_6H_5)_3)_2Br_2$ was isolated. Solution spectra of Ir(*p*-$CH_3C_6H_4P(C_6H_5)_2)_2COI(SO_4)$ were obtained in $CHCl_3$ without difficulty.

Acknowledgment.—We are pleased to acknowledge support from the National Institutes of Health—Air Pollution Section, Grant No. AP 00794-01; the National Science Foundation, Grant No. GP 9101; the Petroleum Research Fund, Grant No. 3635-C3; and a grant from the Center for Materials Research. We are also indebted to Jack R. Norton for helpful discussions.

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