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A Kinetic and Mechanistic Study of the Formation of Iridium(III) Ozonide Complexes by the Insertion of Hexafluoroacetone into Complexes IrX(CO)L₂O₂ (X = Halogen, L = Substituted Phosphine or Arsine)

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Abstract: Synthetic and kinetic studies on the formation of iridium(III)ozonide complexes from the addition reaction of compounds IrX(CO)L₂O₂ with hexafluoroacetone are reported. Complexes IrX[O₃C(CF₃)₂](CO)L₂ (L = PPh₃; X = Cl, Br, I; L = AsPh₃, PMePh₂, P(*p*-tolyl)₃, P(*p*-anisyl)₃; X = Cl) have been characterized. The reaction follows the rate law rate = k[IrX(CO)L₂O₂][CF₃COCF₃]. For L = PPh₃, the rate of reaction follows the sequence for X of Cl > Br > I. For the compound with X = Cl, the relative rates for changing L are AsPh₃ ~ PMePh₂ > PPh₃. First-order rate constants with L = PPh₃ and X = Cl, Br, I are reported using benzene, acetonitrile, and 3-pentanone solvent systems. For the case of the compound IrCl(CO)(PPh₃)₂O₂ the rate is not diminished by the presence of added chloride ion or triphenylphosphine. The results are interpreted on the basis of a mechanism involving direct electrophilic attack of the hexafluoroacetone on the coordinated oxygen molecule to give the iridium(III) ozonide product via an ionic transition state.

Recently we have found that the hexametallic cluster compound Rh₆(CO)₁₆ can be used as a homogeneous catalyst for the oxidation of carbon monoxide to carbon dioxide and also of ketones to carboxylic aicds.[1] Subsequently we have found that this catalytic oxidation of ketones can also be effected with the complexes Pt(PPh₃)₂O₂ and IrCl(CO)(PPh₃)₂.[2] It was concluded in this study that the catalytic oxidation is a free-radical autoxidation process. In this metal-catalyzed reaction carbon-carbon bond cleavage occurs and a mixture of acids can be formed. While this study was in progress, other workers reported the surprising result that these platinum and iridium complexes were homogeneous catalysts for the oxidation of aldehydes to carboxylic acids by a non-free-radical mechanism.[3] These authors made the tentative suggestion that the intermediate in this oxidation reaction was a metalloozonide type complex 1, previously obtained by treating the compound Pt(PPh₃)₂O₂ with aldehydes. Similar type complexes have also been obtained from treating this platinum oxygen compound with a range of ketones[4,5,6] and

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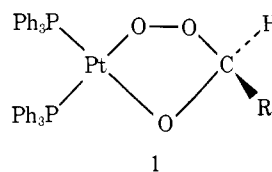
diketones.[7] A mechanism for this reaction has been proposed involving initial coordination of the aldehyde or ketone to the coordinately unsaturated complex Pt(PPh₃)₂O₂, followed by insertion into the metal-oxygen bond to form the platinum-ozonide product. Such a proposal is interesting in view of our observation of a similar catalytic reactivity of both IrCl(CO)(PPh₃)₂O₂ and Pt(PPh₃)₂O₂, since such a pathway is not feasible for the coordinately saturated iridium complex. It is therefore of interest to us to investigate whether the complex IrCl(CO)(PPh₃)₂O₂ will react with aldehydes or ketones to form an iridium(III)-ozonide insertion product of the type obtained with the platinum complex. We have found that such

Table I. Rate Constant Data for the Reaction $IrX(CO)L_2O_2 +$
$(CF_3)_2CO \rightarrow IrX[O_3C(CF_3)_2](CO)L_2$

X	L	Solvent (v/v)	k_{obsd}, s^{-1}
Cl	PPh$_3$	C_6H_6/CH_2Cl_4 (4:1)	9.77×10^{-4}
Br	PPh$_3$	C_6H_6/CH_2Cl_2 (4:1)	2.72×10^{-4}
I	PPh$_3$	C_6H_6/CH_2Cl_2 (4:1)	$<10^{-5}$
Cl	PPh$_3$	CH_3CN/CH_2Cl_2 (1:1)	$>10^{-2}$
Br	PPh$_3$	CH_3CN/CH_2Cl_2 (1:1)	2.17×10^{-3}
I	PPh$_3$	CH_3CN/CH_2Cl_2 (1:1)	2.43×10^{-4}
Cl	PPh$_3$	3-Pentanone/CH_2Cl_2 (1:1)	$>10^{-2}$
Br	PPh$_3$	3-Pentanone/CH_2Cl_2 (1:1)	1.52×10^{-3}
I	PPh$_3$	3-Pentanone/CH_2Cl_2 (1:1)	1.68×10^{-3}
Cl	AsPh$_3$	C_6H_6/CH_2Cl_2 (4:1)	$\gg 10^{-2}$
Cl	PMePh$_2$	C_6H_6/CH_2Cl_2 (4:1)	$\gg 10^{-2}$

a reaction will occur with the activated ketone hexafluoroacetone. The purpose of this paper, therefor, is to present our kinetic data on this reaction, and to use the information to conclude a likely mechanism for the reaction.

Results and Discussion

When the complexes $IrX(CO)L_2O_2$ (X = Cl, Br, I; L = PPh$_3$, X = Cl; L = AsPh$_3$, PMePh$_2$, P(C$_6$H$_4$Me-p)$_3$, P(C$_6$H$_4$OMe-p)$_3$) are treated with hexafluoroacetone the insertion compounds **2** are formed in high yield (eq 1). These

$$IrX(CO)L_2O_2 + CF_3COCF_3 \longrightarrow$$

2 (1)
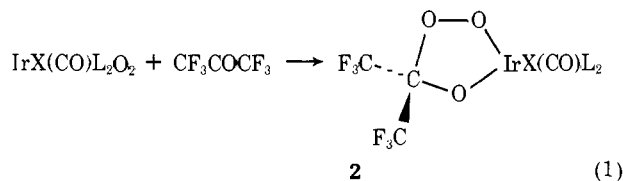
new complexes are colorless or pale green in color, and show values for ν(CO) in the vicinity of 2050 cm^{-1}. This band position is in the region expected for an iridium(III) carbonyl complex. If we assume that the ligands L in the complex **2** are mutually trans, there are two possible isomers for complex **2**. These arise from the feasibility of having carbonyl or chloride ligands trans to the different oxygens. Because of the close similarity between these ligating oxygens we cannot spectroscopically identify the precise stereochemistry of the complexes. Except for the case of the complex IrI(CO)(P-Ph$_3$)$_2$[O$_3$C(CF$_3$)$_2$] only one isomer is formed and we have measured the rate of the reaction shown in eq 1. Rate data have been obtained at 22 °C by following the rate of appearance of the carbonyl peak of the product in the 2000–2100-cm^{-1} region of the infrared spectrum.[8] The observed rate law is shown in the equation

$$\text{rate} = k[IrX(CO)L_2O_2][CF_3COCF_3] \qquad (2)$$

This shows that the rate of the reaction is first order in each reactant. Kinetic measurements have been made under pseudo-first-order conditions with hexafluoroacetone present in large excess, and these pseudo-first-order rate constants are shown in Table I. These data show that the rate of the reaction is dependent on the halide X, the neutral ligand L, and the nature of the solvent. The halogen dependency of the reaction rate follows the sequence Cl > Br > I, and the observed sequence for the ligands L is PMePh$_2$ ~ AsPh$_3$ > PPh$_3$. We have been unable to extend the halide sequence to the fluoro complex since the oxygen adduct is insufficiently stable to oxygen dissociation, and impure materials result from the reaction with hexafluoroacetone. Also from Table I it is apparent that the reaction proceeds at a faster rate in the presence of the more strongly coordinating, high dielectric constant solvents, 3-pentanone and acetonitrile.[9] In contrast to the reaction of Pt(PPh$_3$)$_2$O$_2$ with ketones, we have found that the complex IrCl(CO)(PPh$_3$)$_2$O$_2$ will only react to completion with the

highly activated ketone hexafluoroacetone. The iridium(III) ozonide complexes obtained from this addition reaction (eq 1) are robust, and it is significant to the interpretation of the kinetic data that refluxing a solution of the complex in benzene for 1 h causes no significant elimination of hexafluoroacetone.

A possible reaction pathway which has been considered is one where the insertion reaction is preceded by dissociation of one of the ligands from the compound IrCl(CO)(PPh$_3$)$_2$O$_2$. We have therefore investigated the effect of the addition of excess triphenylphosphine or chloride ion on the rate of reaction with hexafluoroacetone. In neither case do we find any inhibition of the reaction rate in the presence of these species; indeed the addition of triphenylphosphine may cause a slight acceleration of the reaction, although the magnitude of the increase is within the error limits of the rate data shown in Table I. An additional problem in the interpretation of this effect of added triphenylphosphine is the knowledge that hexafluoroacetone and triphenylphosphine react rapidly at -70 °C to form a phospholane adduct.[10] In view of this additional reaction it is therefore significant that the iridium(III) ozonide complex formed by the reaction shown in eq 1 is formed in essentially quantitative yield.[11] If dissociation of triphenylphosphine was a significant step in the reaction, the free ligand would be converted to phospholane by the excess hexafluoroacetone, and a reduced yield of iridium(III) ozonide would result.

The kinetic data shown in Table I, along with the inhibition studies, can be best interpreted in terms of a mechanism involving direct electrophilic attack of the activated ketone on the coordinated oxygen molecule. The reaction rate is first order in both hexafluoroacetone and the compound IrX(CO)-L$_2$O$_2$, and the rate dependence on concentration of hexafluoroacetone is shown in Figure 1. This result indicates a bimolecular transition state, and the dependence of reaction rate on dielectric constant of the solvent system shows that an ionic transition state is involved in the reaction. We propose that a reaction pathway resembling that shown in eq 3 reasonably

(3)
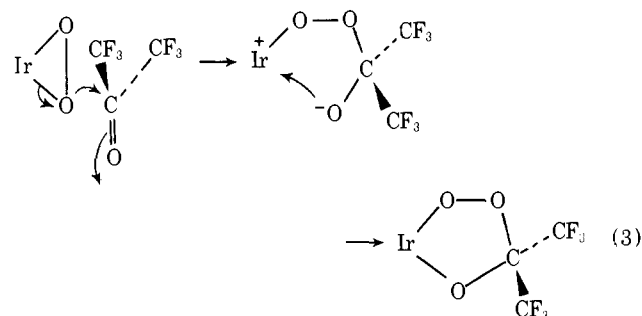
represents the mechanism for the reaction. We find no evidence for the formation of any intermediate, and the middle structure in eq 3 does not in any way represent a species having s significant lifetime. Such a mechanistic pathway is supported by the halide X, ligand L, and solvent effects on the reaction rate. In kinetic studies on the oxidative addition of methyl iodide to IrX(CO)(PPh$_3$)$_2$ it has been shown that the rate of the reaction follows the sequence for dependence on halogen X of Cl > Br > I.[12,13] This result shows that the "electronegativity" of the three halogens to iridium(I) is reversed from that found in bonding to hy rogen, and the chlorocarbonylbis(triphenyl-phosphine)iridium(I) complex is the most nucleophilic of the three compounds. This trend is reversed in the reactivity of these haloiridium(I) complexes to hydrogen or oxygen, or in the reaction of O$_2$ with a coordinated nitrosyl,[14] but it appears that our results show a similar halogen dependence to that observed for methyl iodide addition. It may be pertinent that in this addition reaction of hexafluoroacetone with a coordi-

nated oxygen molecule, there is a smaller contribution from steric effects. The rate dependence on ligand L also correlates with electrophilic attack on the coordinated oxygen since earlier equilibrium studies on complexes $IrCl(CO)L_2$ have shown that when triphenylphosphine is substituted for either triphenylarsine or methyldiphenylphosphine there is a corresponding increase in the electron density[15] and basicity[16] on iridium(I). Our kinetic data on the reaction of hexafluoroacetone with complexes $IrX(CO)L_2O_2$ represent one of the few studies giving information regarding reactivity patterns of coordinated π-acceptor ligands to electrophilic attack, and it is apparent that electronic effects on the metal center from ligands L and X are also transmitted to the coordinated oxygen. From considerations of comparable complexes of cobalt, rhodium, iridium, and platinum, it appears that oxygen is a strong π-acceptor ligand comparable to tetrafluoroethylene in its donor-acceptor properties. It is to be anticipated therefore that electron-releasing ligands on iridium will cause the coordinated oxygen to be susceptible to attack by electrophiles.

A recent kinetic study has been made on a similar insertion reaction of ketones with the complex $Pt(PPh_3)_2O_2$.[17] These authors have verified the original suggestion that the mechanism involves initial coordination of the ketone to the vacant coordination site on the metal followed by insertion to form the platinum–ozonide complex. Such a mechanistic pathway is not possible for the coordinately saturated complex $IrX(CO)L_2O_2$, and it is very unlikely that a poorly coordinating ligand such as hexafluoroacetone will form a 20-electron molecule as intermediate. It is conceivable, however, that the initial step in the reaction involves dissociation of a halide ion, or of a triphenylphosphine or carbon monoxide molecule. Our results show that the addition of a 1000:1 mole ratio of LiCl:IrCl(CO)(PPh_3)_2 causes no observable diminution of rate of the insertion reaction, and that twofold increase of rate is observed on addition of triphenylphosphine in a mole ratio of 10:1 for PPh_3:$IrBr(CO)(PPh_3)_2$. These data indicate that dissociation of these ligands is not involved in a slow step of the reaction. These kinetic data have been obtained under pseudo-first-order conditions with a saturated solution of hexafluoroacetone. It is significant to the inhibition studies to know the solubility of hexafluoroacetone. We have made an estimate of this quantity for a solution of hexafluoroacetone in benzene at 22 °C. The value of 2.86 (2) for the Bunsen coefficient represents a ratio of between 10:1 and 15:1 for the concentrations of hexafluoroacetone:$IrX(CO)L_2O_2$ used in the kinetic runs. Since this ratio is small compared to the mole ratio of 1000:1 chloride:$IrCl(CO)(PPh_3)_2O_2$ used in one inhibition experiment, and is not significantly greater than the ratio of triphenylphosphine:$IrCl(CO)(PPh_3)_2O_2$ used in the other, we consider our inhibition experiments to be valid even under the pseudo-first-order conditions used in the kinetic runs. We consider it yery unlikely that predissociation of carbon monoxide will occur. A single carbonyl group bonded to iridium(I) is expected to be strongly coordinated because of considerable π bonding between the metal and ligand. Additionally, the low solubility of carbon monoxide in benzene[18] would cause even small quantities of free carbon monoxide to be expelled from the solution by the slow stream of hexafluoroacetone. Such a stream of reactant is passed through in order to keep the reaction conditions as close to pseudo-first-order as possible. Any removal of carbon monoxide from solution would cause a decreased yield of product.

An alternate mechanistic pathwya which must be considered is one involving initial dissociation of oxygen from the complex $IrCl(CO)(PPh_3)_2O_2$. Such a route could involve complete dissociation of oxygen (eq 4), or could occur via a conversion of the oxygen coordination from side-on to end-on, with a subsequent rapid trapping of this intermediate by hexafluo-
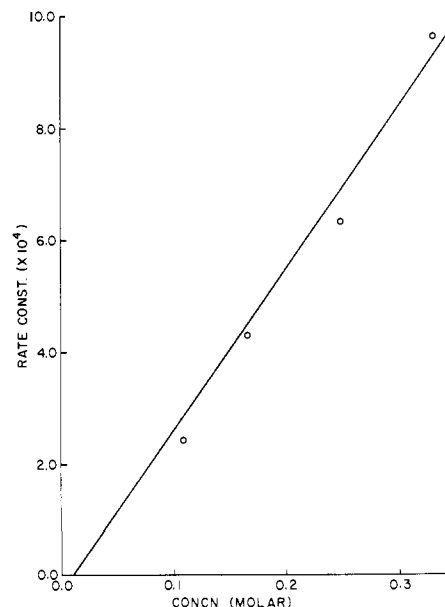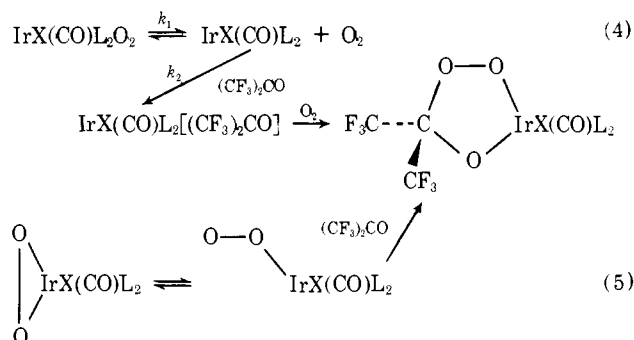

Figure 1. Plot of rate constant against concentration of hexafluoroacetone for reaction 1 (X = Br; L = PPh_3).

roacetone to give product (eq 5).[19] The pathway outlined in eq 4 can be eliminated since first-order rate constants k_1 have

$$IrX(CO)L_2O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} IrX(CO)L_2 + O_2 \qquad (4)$$

been previously reported by Vaska's group,[20] and we have measured the pseudo-first-order rate constant k_2. The value k_1 for the complex $IrCl(CO)(PPh_3)_2O_2$ is 1.38×10^{-5} at 40 °C, and for the reaction shown in eq 6 we find a value of 4×10^{-5} s^{-1}. It is significant to the elimination of the mechanism outlined in eq 4 that the values for k_1 and k_2 are each two orders of magnitude slower than we have found for the formation of the iridium(III) ozonide compound from the oxygen adduct. The hexafluoroacetone adduct (eq 6) has previously been
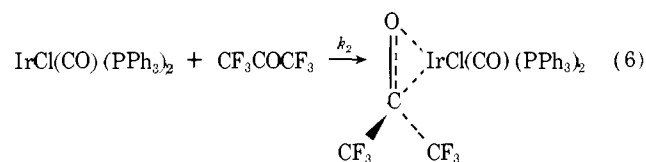
prepared by Stone et al. using this synthetic route, but no kinetic data were reported.[21] It is an interesting observation that hexafluoroacetone reacts with the coordinated oxygen at a rate two orders of magnitude faster than is found for the direct addition of hexafluoroacetone to the iridium(I) metal center.

The pathway shown by eq 5 involving a two-step mechanism for oxygen dissociation is more plausible because the observed rate order Cl > Br > I found for oxidative addition of hexafluoroacetone to $IrX(CO)L_2O_2$ is also the one followed for dissociation of oxygen. This resulting product from this route is identical with the one involving direct electrophilic attack on the coordinated oxygen in that the oxygen–oxygen bond
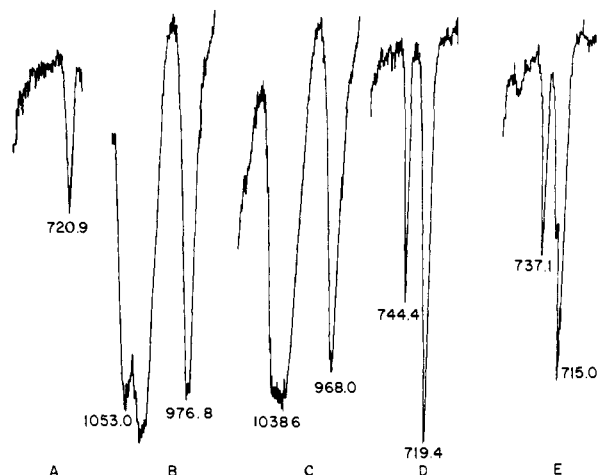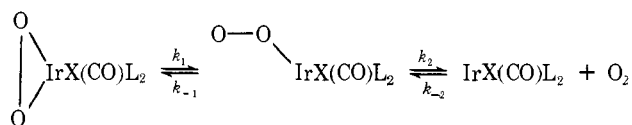
Figure 2. Infrared labeling study from $IrCl(CO)[P(C_6H_4OMe\text{-}p)_3]_2{}^{18}O_2$ and hexafluoroacetone: A, $IrCl(CO)[P(C_6H_4OMe\text{-}p)_3]_2O_2$; B, D, $IrCl(CO)[P(C_6H_4OMe\text{-}p)_3]_2[O_3C(CF_3)_2]$ (from O_2); C, E, $IrCl(CO)\text{-}[P(C_6H_4OMe\text{-}p)_3]_2[O_3C(CF_3)_2]$ (from $^{18}O_2$).
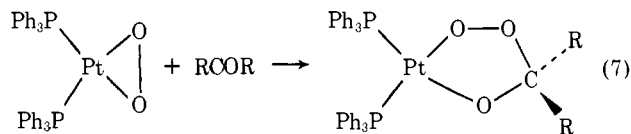
again remains intact on product formation. Earlier workers have carried out an ^{18}O labeling study on the reaction of sulfur dioxide with the complex $IrCl(CO)(PPh_3)_2O_2$ and have concluded that the O–O bond remains unbroken in the primary step of the reaction.[22] The significant data which lead to doubt about this mechanism (eq 5) involving a unimolecular isomerization step are both the rate data for the triphenylarsine and methyldiphenylphosphine complexes and the observation that the reaction rate is first order in hexafluoroacetone. Since both methyldiphenylphosphine and triphenylarsine increase the electron density at iridium, the rate of dissociation of oxygen is slowed,[20] and the overall reaction leading to formation of product is expected to decrease. The observed rate increase with the triphenylarsine and methyldiphenylphosphine complexes, however, precludes this mechanism, but supports the one involving direct electrophilic attack on the coordinated oxygen. Our results were therefore in agreement with the suggestion of Vaska's group that there is no evidence for the idssociation of oxygen occurring in a stepwise manner.[20] In order to accommodate our data into a mechanism involving a side-on bonded superoxo complex as intermediate it will be necessary to make some assumptions about the dissociation of oxygen from complexes $IrX(CO)L_2O_2$. We need to propose

$$\begin{array}{c}O\\ \big| \diagdown \\ \big| \diagup \\ O\end{array} IrX(CO)L_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{array}{c}O\!-\!O\\ \diagdown\end{array} IrX(CO)L_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} IrX(CO)L_2 + O_2$$

that in the sequence shown below the rates k_1 and k_{-1} are fast and the slow step (k_2) in the dissociation is the breaking of the secon diridium–oxygen bond. This would lead to the conclusion that our rate data for $L = PMePh_2$ and $AsPh_3$ give us information which can only be compared with the second equilibrium, and not with the formation of a superoxo intermediate. The overall order of the reaction with hexafluoroacetone would arise from a slow step involving reaction between the ketone and this end-on bonded intermediate. It is important to realize that it is a requirement of this mechanism that the ketone attacks at the free oxygen as an electrophile, and not at the now coordinately unsaturated iridium center as a ligand. This detail is made necessary by our observation that the rate of the reaction is not inhibited by added excess ligand such as halide ion. We appreciate that our data do not entirely eliminate a mechanism having an end-on bonded oxygen intermediate, but consider that this latter restriction is a rather severe one. Nevertheless we do not completely discount the possibility of

such a route, and emphasize that it is mainly from the lack of any direct evidence for an intermediate with an end-on bonded oxygen that we conclude that our data are best explained by a mechanism involving direct electrophilic attack of the ketone on the side-on bonded oxygen.

Since completion of the major portion of this work, a group of researchers have made a kinetic study of the insertion reaction of ketones into the compound $Pt(PPh_3)_2O_2$ to form the platinum(II) ozonide complexes (eq 7)[17] These authors pro-

$$\underset{\substack{\diagup \\ Ph_3P}}{\overset{\substack{Ph_3P \\ \diagdown}}{Pt}}\!\!\begin{array}{c}O\\ \diagup \\ \big| \\ \diagdown \\ O\end{array} + RCOR \longrightarrow \underset{\substack{\diagup \\ Ph_3P}}{\overset{\substack{Ph_3P \\ \diagdown}}{Pt}}\!\!\begin{array}{c}O\!\!-\!\!O\\ \diagdown \\ \diagup \\ O\end{array}\!\!\!\!\begin{array}{c}R\\ \diagup \\ C\\ \diagdown \\ R\end{array} \qquad (7)$$

pose a two-pathway mechanism. The faster route is a bimolecular one involving initial coordination of the ketone to the vacant coordination site on platinum, followed by insertion into the metal–oxygen bond to give product. The second pathway suggested by these authors to be operable is one following a unimolecular first-order rate law which is independent of ketone concentration. This reaction with platinum proceeds at a much faster rate than does the corresponding reaction with iridium oxygen complexes. The ozonide complexes of platinum(II) can be formed with a much broader range of ketones,[5-7] and for carrying out kinetic measurements even the addend trifluoroacetone proceeds at a rate which is too fast to be measured. Our results from this work show that the second pathway cannot be the mechanism found for us with the $IrX(CO)L_2O_2$ complexes, since this route is also a bimolecular one with a first-order dependence on ketone. The plausible unimolecular pathway for the slow route is the one considered by us as arising from an initial isomerization of the coordinated oxygen. Nevertheless such a pathway appears to be too slow to be detected for the iridium oxygen complexes, and if this is indeed the slower pathway for the platinum complex the rate of partial dissociation of oxygen from $Pt(PPh_3)_2$ must be faster than from $IrCl(CO)(PPh_3)_2$.

We have prepared the isotopically labeled complex $IrCl(CO)[P(C_6H_4Me\text{-}p)_3]_2{}^{18}O_2$ using 99% enriched oxygen.[23] This compound has been treated with hexafluoroacetone to give the cyclic ozonide complex 2 with two of the three oxygen atoms in the ring labeled. The infrared spectrum of this product is compared with that of unlabeled complex 2 in Figure 2. From the sequence of spectra it is apparent that new bands appear on conversion of the oxygen adduct into complex fb2, and that these bands shift when labeled oxygen is incorporated. Upon formation of the hexalfuoroacetone insertion product 2 new bands appear at 1053.0, 976.8, 744.4, and 719.4 cm^{-1} (spectra b and d). In spectra c and e of the isotopically labeled adduct these bands shift to 1038.6, 968.0, 737.1, and 715.0 cm^{-1}. The third band in spectrum e is at 720.9 cm^{-1} and is apparently a phosphine band present in all these complexes (see spectrum a), but in the unlabeled sample of 2 is not resolved from the band at 719.4 cm^{-1}. In Scheme I is shown schema-

Scheme I
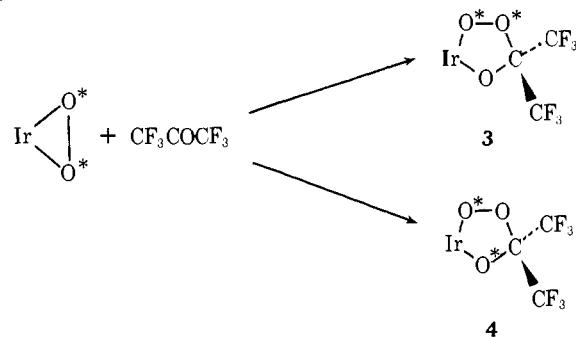
tically the products **3** and **4** arising from insertion of hexafluoroacetone into the Ir-O and O-O bonds, respectively, of complexes $IrCl(CO)L_2(O_2)$. If any of these bands are primarily of O-O character we would anticipate that these would be shifted by up to 40 cm^{-1} in **3** and up to 20 cm^{-1} in **4**. From the observed shifts it is apparent that no bands can be assigned to $\nu(O+-O^*)$. The most reasonable assignments for bands of these positions and intensities are that the higher energy bands are primarily due to $\nu(C-O)$,[24] and the lower energy bands are assigned as $\delta(C-O)$. In either **3** or **4** we will have vibrations due to both C-O and C-O*. An analysis of Figure 2 leads to the assignments 1038.6 cm^{-1}, $\nu(C-O^*)$; 737.1 cm^{-1}, $\delta(C-O^*)$; 968.0 cm^{-1}, $\nu(C-O)$; 715.0 cm^{-1}, $\delta(C-O)$. This corresponds to a shift in $\nu(C-O^*)$; of 14.4 cm^{-1} and in $\delta(C-O^*)$ of 7.3 cm^{-1}. This shift is smaller than calculated from a diatomic simple harmonic oscillator model because of the coupling of the modes in the cyclic structure. This vibronic coupling is further shown by shifts in $\nu(C-O)$ and $\delta(C-O)$ of 8.8 and 4.4 cm^{-1}, respectively, in the labeled product. The distinction between **3** and **4** depends on the assignment of the two different sets of C-O modes to the chemically different C-O groups in the product. Since one of these oxygens is coordinated to iridium it is to be expected that the contribution to the reduced mass will cause this C-O group to be at lower energy than the other one. Since in each case the higher energy bond in the pair is the one which shows the greater shift, this is therefore a C-O* mode. This leads to the conclusion that **3** is the preferred structure for the labeled adduct.

Experimental Section

Physical Measurements. Kinetic data were recorded on a Beckman IR-4 infrared spectrometer using sodium chloride cells having a path length of 0.05 mm. Infrared spectra of new complexes were measured on a Perkin-Elmer Model 700 spectrometer as Nujol mulls. Melting points were obtained on a Fischer-Johsn melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

Materials. Iridium(I) complexes were prepared by known procedures.[19a] Benzene was dried over calcium hydride and distilled. Acetonitrile was distilled from anhydrous copper sulfate. 3-Pentanone was dried over phosphorus pentoxide and distilled. Dichloromethane was reagent grade (<0.02% water) and used without prior purification. Hexafluoroacetone was purchased from PCR Inc., Gainesville, Fla., and passed through Drierite prior to use.

Kinetic Data. Kinetics of the addition reaction were followed by measuring the growth of the product carbonyl stretching frequency in the 2050-cm^{-1} range. A baseline method was used to measure peak height, and an assumption was made that the peak height was proportional to absorbance. This assumption was considered to be valid since the peak is sharp (width of half-height of 20 cm^{-1}) and the greatest intensity is never more than 90% transmittance. The peak height was measured in millimeters and ln $(1 - PH_t/PH_\infty)$ against time in seconds plotted (PH_t is the peak height at time t and PH_∞ is the peak height after a minimum of 6 half-lives). The plots obtained were linear for at least 2 half-lives. All kinetic runs were made under pseudo-first-order conditions where the initial ratio of the molar concentration of hexafluoroacetone:iridium oxygen complex is in the region of 15:1. This ratio increased during the reaction since the hexafluoroacetone which had reacted during the kinetic run was continuously replaced by bubbling the gas through the solution in order to maintain saturation. Times were measured at the instant the instrument recorder registered the lowest level of transmittance. Samples were taken from the reaction mixture for concentration measurements but we consider that the high solubility of hexafluoroacetone in the solvents precludes any significant error caused by degassing of this reactant. The reaction vessel was thermostated to 22.0 ± 0.01 °C using a Sargent thermometer and a water bath.

The measurements made to obtain the reaction order in hexafluoroacetone were carried out in a glass pressure vessel of approximate volume 85 mL. The vessel was fitted with a septum in order that solution samples could be extracted with a long needle and gas syringe. The reaction vessel was again thermostated and samples withdrawn

into the syringe were partially degassed to avoid bubbles in the infrared cells. Times were recorded using a similar procedure to the atmospheric pressure measurements. All concentrations of iridium oxygen complexes were in the range of 5.00-8.00 × 10^{-3} M. Solubility measurements in hexafluoroacetone were made using apparatus similar to that previously described.[25]

Isotopically labeled $^{18}O_2$ (99%) was obtained from Stohler Isotopes Inc. The labeling experiment was performed by attaching the ampule (100 mL) to a capillary diameter vacuum line to which was attached a small round-bottomed flask. The total volume of the apparatus and ampule was approximately 110 mL.

Chloro[bis(trifluoromethyl)ozonide]carbonylbis(triphenylphosphine)iridium(III), IrCl[O$_3$C(CF$_3$)$_2$]CO(PPh$_3$)$_2$. A 50-mL three-necked flask was equipped with a Nujol-filled bubble tube and dry ice condenser. A gas inlet tube was fitted into the third neck and a Teflon-covered stir bar inserted. Benzene (15 mL) was added to the flask and then the compound $IrCl(CO)(PPh_3)_2$ (0.1 g). After solution, oxygen gas was passed in through the inlet tube for 7 h, during which time the solution changed to a pale orange color and a precipitate formed. A dry ice-acetone slush was placed in the condenser and hexafluoroacetone was passed into the flask until initiation of refluxing. After 10 min from the beginning of hexafluoroacetone addition the color changed from orange to a yellow-green color. The solvent benzene was then removed under reduced pressure leaving a green oil. Addition of diethyl ether gave the complex as a green precipitate which was filtered and dried in air: yield 0.075 g (58%); mp 190 °C dec; ν_{max} (as a KBr pellet) 2050 vs (νCO), 1300 m (νCF), 1285 m (νCF), 1225 s (νCF), 1210 vs (νCF), 1140 vs (νCF), 1050 vs (νCF), 978 cm^{-1} vs. Anal. Calcd for $C_{40}H_{30}ClF_6IrO_4P_2$: C, 49.1; H, 3.09; F, 11.7. Found: C, 49.2; H, 3.09; F, 11.4.

Iodo[bis(trifluoromethyl)ozonide]carbonylbis(triphenylphosphine)iridium(III), IrI[O$_3$C(CF$_3$)$_2$]CO(PPh$_3$)$_2$. Again using a similar synthetic procedure the complex is obtained as a yellow powder. The reaction time for the hexafluoroacetone insertion reaction was increased to 6 h: ν_{max} (KBr pellet) 2050 s (νCO), 1300 sh (νCF), 1280 m (νCF), 1260 m (νCF), 1260 m (νCF), 1220 s (νCF), 1130 s (νCF), 1040 s (νCF), 970 cm^{-1} (s). Anal. Calcd for $C_{40}H_{30}F_6IIrO_4P_2$: C, 44.9; H, 2.83; F, 10.7. Found: C, 45.0; H, 2.94; F, 10.5.

Bromo[bis(trifluoromethyl)ozonide]carbonylbis(triphenylphosphine)iridium(III), IrBr[O$_3$C(CF$_3$)$_2$]CO(PPh$_3$)$_2$. A similar synthetic procedure with 0.075 g was used as described for the chloro complex except that now the reaction time after addition of hexafluoroacetone was increased to 3 h: yield 0.067 g (75%); ν_{max} (KBr pellet) 2050 vs (νCO), 1300 m (νCF), 1285 m (νCF) 1230 s (νCF), 1205 s (νCF), 1140 s (νCF), 1045 s (νCF), 975 cm^{-1} s. Anal. Calcd for $C_{40}H_{30}BrF_6IrO_4P_2$: C, 47.0; H, 2.96; F, 11.1. Found: C, 46.9; H, 2.91; F, 11.0.

Chloro[bis(trifluoromethyl)ozonide]carbonylbis(methyldiphenylphosphine)iridium(III), IrCl[O$_3$C(CF$_3$)$_2$]CO(PMePh$_2$)$_2$. Hexafluoroacetone was bubbled through a solution of the compound IrCl(CO)(PMePh$_2$)$_2$O$_2$ (0.1036 g) in dichloromethane (5 mL) for 5 min. The color of the solution changed from brown to pale green. The solution was filtered through Celite and the solvent removed on a rotary evaporator with a water aspirator. Ether, then hexane, was added to the resulting green oil to give the complex as a light green precipitate. This compound was washed with hexane, filtered, then dried in vacuo: yield 0.1001 g (78%); mp 174-175 °C; ν_{max} (Nujol mull) 2050 vs (νCO), 1290 m (νCF), 1225 s (νCF), 1205 s)νCF), 1190 sh (νCF), 1150 vs (νCF), 1140 vs (νCF), 1040 vs (νCF), 970 vs, 710 cm^{-1} ms (δCO). Anal. Calcd for $C_{30}H_{26}ClF_6IrO_4P_2$: C, 42.2; H, 3.07; F, 13.4. Found: C, 42.4; H, 3.11; F, 13.2.

Chloro[bis(trifluoromethyl)ozonide]carbonylbis(triphenylarsine)iridium(III), IrCl[O$_3$C(CF$_3$)$_2$]CO(AsPh$_3$)$_2$. Using a similar procedure as for the methyldiphenylphosphine complex with IrCl(CO)(AsPh$_3$)$_2$O$_2$ (0.1054 g) the complex was obtained as a light green solid: yield 0.1046 g (84%); mp 169-173 °C; ν_{max} (Nujol mull) 2050 vs (νCO), 1310 m (νCF), 1300 m (νCF), 1230 s (νCF), 1210 s (νCF), 1200 sh (νCF), 1050 m (νCF), 980 s, 720 cm^{-1} ms (δCO). Anal. Calcd for $C_{40}H_{30}As_2ClF_6IrO_4P_2$: C, 45.1; H, 2.84; F, 10.7. Found: C, 44.8; H, 3.07; F, 10.4.

Chloro[bis(trifluoromethyl)ozonide]carbonylbis(tri-p-tolylphosphine)iridium(III), IrCl[O$_3$C(CF$_3$)$_2$]CO[P(C$_6$H$_4$Me-p)$_3$]$_2$. Again using a similar procedure as for the methyldiphenylphosphine complex except that hexafluoroacetone was added slowly over a period of 30 min, the complex was obtained as a light green solid: mp 177-181 °C; ν_{max} (Nujol mull) 2050 vs (νCO), 1300 m (νCF), 1280 m (νCF), 1220

s (νCF), 1140 s (νCF), 1050 s (νCF), 970 s, 735 cm^{-1} m (δCO). Anal. Calcd for C$_{46}$H$_{42}$ClF$_6$IrO$_4$P$_2$: C, 52.0; H, 3.99; F, 10.7. Found: C, 52.1; H, 4.03; F, 10.5.

Chloro[bis(trifluoromethyl)ozonide]carbonylbis(tri-*p*-anisylphosphine)iridium(III), IrCl[O$_3$C(CF$_3$)$_2$]CO[P(C$_6$H$_4$OMe-*p*)$_3$]$_2$. To the complex IrCl(CO)[P(C$_6$H$_4$OMe-*p*)$_3$]$_2$ (50 mg) was added dry benzene (5 mL). Oxygen was bubbled through the solution until the color changed from yellow to orange (~2 h). Through this solution of the oxygen adduct was passed hexafluoroacetone for 30 min when the color of the solution had changed to green. The solvent was removed in vacuo and a mixture of ether and hexane (1:1) added to give a pale green precipitate. The complex was filtered and then dried in vacuo: yield 51.4 mg (85%); mp 163-165 °C; ν_{max} (Nujol mull) 2050 vs (νCO), 1225 s (νCF), 1200 s (νCF), 1140 s (νCF), 1045 sh (νCF), 970 s, 720 cm^{-1} m (δCO). Anal. Calcd for C$_{46}$H$_{42}$ClF$_6$IrO$_{10}$P$_2$: C, 47.7; H, 3.66; F, 9.84. Found: C, 47.5; H, 4.17; F, 9.88.

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(19) It appears likely that the mechanism outlined in eq 5 can be eliminated by consideration of our data in conjunction with that published previously.[20] Assuming that intermediate B is formed in the addition of hexafluoroacetone to A, we obtain the following:

$$\frac{d(B)}{dt} = k_1[A] - k_{-1}[B] - k_2[B][(CF_3)_2CO] = 0$$

$$k_1[A] = k_{-1}[B] + k_2[B][(CF_3)_2CO]$$

therefore

$$\frac{k_1[A]}{k_{-1} + k_2[(CF_3)_2CO]} = [B]$$

since

$$\frac{dC}{dt} = k_2[B][(CF_3)_2CO]$$

$$= \frac{k_1 k_2[A][(CF_3)_2CO]}{k_{-1} + k_2[(CF_3)_2CO]}$$

Since we find the reaction to be first order in hexafluoroacetone, one must assume that $k_{-1} \gg k_2$. Hence

$$\frac{dC}{dt} = \frac{k_1 k_2[A][(CF_3)_2CO]}{k_{-1}}$$

From previous work[19] we can assume that k_1 approximates the value 7.5 $\times$ 10^{-7} (30 °C) found for the dissociation of O$_2$ from IrBr(CO)(PPh$_3$)$_2$O$_2$; k_{-1} approximates the value 0.130 (30 °C) found for the association of O$_2$ with IrBr(CO)(PPh$_3$)$_2$. In the case of IrBr(CO)(PPh$_3$)$_2$O$_2$ in benzene at 22 °C, k_{obsd} = 2.72 $\times$ 10^{-4} s^{-1}. Since

$$\frac{k_1 k_2}{k_{-1}}[(CF_3)_2CO] = k_{obsd}$$

therefore

$$k_2 = (2.72 \times 10^{-4})\frac{k_{-1}}{k_1[(CF_3)_2CO]}$$

Since

$$[(CF_3)_2CO] = 0.109$$

$$k_2 = (2.50 \times 10^{-3})\frac{k_{-1}}{k_1} = \frac{(2.50 \times 10^{-3})(0.130)}{7.5 \times 10^{-7}} = 433$$

therefore $k_2[(CF_3)_2CO]$ = (433)(0.109) = 47.1. Since the assumption that $k_{-1} \gg k_2$ is not valid, such a mechanism would not show first-order dependence on hexafluoroacetone.

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