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TEMPERATURE-DEPENDENT SULFUR DIOXIDE ADDITION TO SOME IRIDIUM(I) AND RHODIUM(I) COMPLEXES CONTAINING π LIGANDS

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SUMMARY

Reactions are described which involve addition of sulfur dioxide to iridium(I) and rhodium(I) complexes having π ligands coordinated to the metal:

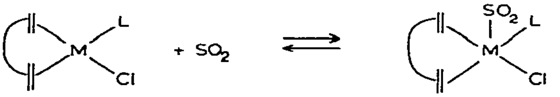
$$[(\text{Diene})\text{MClL}]+\text{SO}_2 \leftrightarrows [(\text{Diene})\text{M}(\text{SO}_2)\text{ClL}]$$

where Diene = 1,5-cyclooctadiene or norbornadiene; $L = P(C_6H_5)_3$ or piperidine and $M = Rh^I$ or Ir^I. The SO_2 adducts are stable at low temperature (~0°) and lose sulfur dioxide on heating. An analogous SO_2 addition is observed with complexes of the type $[Rh(CO)_2LCl]$ with $L = P(C_6H_5)_3$ or piperidine. The new compounds are discussed in terms of the presence of a $M \rightarrow SO_2$ σ bond.

A number of recent papers have dealt with transition metal complexes having SO_2 as a ligand[1-4]. Transition metals in low oxidation state give complexes with SO_2 in which the bond is mainly σ in nature, involving donation of an electron pair from the metal to the acceptor SO_2, as indicated by both molecular structure observations (infrared spectra[1,4,5] and X-ray structures[6,7]) and the chemical reactivity of these complexes. Transition metal complexes containing SO_2 are generally stable, and can be obtained[3] through displacement of a labile ligand by SO_2. Sometimes SO_2 inserts into the σ metal–carbon bond of a transition[8] or post-transition[9] metal complex. The only example of reversible addition of SO_2 to a complex is that reported by Vaska for complexes of the type *trans*-$[M(CO)(PPh_3)_2Cl]$ ($M = Ir^I$ and Rh^I). The formation of adducts with SO_2 is related to the basicity of the central metal, increasing metal basicity enhancing the stability of the $M \rightarrow SO_2$ bond. This may be the reason for the poisoning action often displayed by SO_2 in catalyzed processes on metal surfaces, in which the metal can be thought of as having an "infinite baisicity". In this context a study of the relationship between metal electron density and $M \rightarrow SO_2$ stability has a particular interest.

We have examined some addition reactions of SO_2 with rhodium(I) and irridium(I) complexes bearing π-ligands, L, such as diolefin and carbon monoxide.

We have found that complexes of type [M(diene)LCl] react under mild conditions with SO_2 gas at 1 atm to give a pentacoordinate adduct with a stoichiometric complex/SO_2 ratio of 1/1. These reactions occur under homogeneous (benzene, chloroform, dichloromethane) and heterogeneous conditions. The uptake of SO_2 depends on temperature: a color change is observed when the solution or the solid complex itself is alternately heated and cooled. The reactions involved are as follows:



(1)

The equilibrium (1) lies far over to the right in heterogeneous conditions, as when SO_2 is taken up by the complexes in the solid at a temperature around $-7°$. For instance solid $[C_8H_{12}RhCl(PPh_3)]$ in a flask connected to a constant pressure gas absorption apparatus at 15° changes color from yellow to red accompanied as SO_2 uptake occurs; this is practically complete after 30 min. The amount of SO_2 taken up corresponds to an SO_2/complex molar ratio of ca. 1.2. The resulting adduct is stable even under vacuum, and is converted to the starting metal complex (identified by IR spectrum and melting point) on heating above 80°. As an example of a reaction in solution, when $[C_7H_8RhCl(PPh_3)]$ (ca. 1 mmole) in 10 ml of benzene is treated at 25° with a stream of SO_2 the yellow solution turns red and a red crystalline solid is precipitated, the elemental analysis of which corresponds with a 1/1 complex/SO_2 adduct.

The IR spectra of the adducts obtained in this way show two absorption bands at ca. 1050 and 1200 cm^{-1}, which can be assigned, respectively, to the symmetric and antisymmetric stretchings of coordinated SO_2. The other bands correspond to those of the initial complex. The stretching frequencies of the SO_2 moiety in these adducts are close to those reported by Vaska for his adducts $[MCl(SO_2)(CO)(PPh_3)_2]$ ($M = Ir^I$ and Rh^I). From the IR spectra, elemental analyses, and SO_2 absorption measurements, we believe that our adducts are pentacoordinated complexes in which coordination of SO_2 to the central metal takes place through the sulfur atom.

Under similar experimental conditions the tetracoordinated complexes containing norbornadiene ligands react more easily than the cyclooctadiene complexes, independent of the nature of the L group. The iridium adducts lose SO_2 less easily than their rhodium analogs, reflecting the greater reluctance of Rh^I compared to Ir^I to enter into oxidative addition reactions[10]. Since the greater stability of the $\sigma\ M \rightarrow SO_2$ bond is related to the metal basicity, the greater tendency of norbornadiene complexes relative to cyclooctadiene to give adducts with SO_2 reflects the more powerful complex forming ability of the former diolefin compared to the latter. This is supported by the fact that whereas complexes of type $[C_7H_8RhClL]$ (with L = phosphine, arsine and stibine) are stable, for the cyclooctadiene analog, only the phosphine compound is stable enough to be isolated[11,12]. Moreover, norbornadiene is the only chelating diolefin known to give complexes with the heaviest elements of the transitional series, as well as with iron and ruthenium. This peculiar coordinating ability of norbornadiene is related to its quasi-conjugated behaviour in organic reactions[13].

The piperidine complexes give SO_2 adducts more easily than their phosphine analogs, suggesting that there is electrophilic attack by SO_2 on the metal, which is made more basic by the coordinated piperidine. A similar trend has been found for the SO_2 insertion reactions in compounds of type $[C_5H_5Fe(CO)(CH_3)L]$: when L = phosphine, the rate of reaction with SO_2 is markedly greater than when L = CO[14].

It is noteworthy in this context that under the experimental conditions described above, no reaction occurs between SO_2 and the cationic complex $[C_8H_{12}Rh(PPh_3)_2]^+$. By contrast, the cationic complex $[Ir(Dppe)_2]^+$ takes up SO_2 to give a stable pentacoordinate adduct[15]. (Dppe = bis(1,2-diphenylphosphino)ethane).

Other reactions examined are the following:

$$[Rh(CO)_2ClL] + SO_2 \leftrightarrows [Rh(CO)_2L(SO_2)Cl] \qquad (2)$$

These proceed in an analogous manner to reaction (1) already described, the complex with L = piperidine again being more reactive than that with phosphine. Further, it appears that rhodium complexes with diolefins are far more reactive than the complexes with two CO groups coordinated. In the chemistry of tetracoordinate planar complexes of d^8 metal ions the ease of introducing a fifth ligand depends on the charge delocalization through π bonding brought about by the other ligands (strong-field ligands) attached to the central metal. Pentacoordination with SO_2 on the other hand, is favored by a greater donation of charge to the metal on the part of highly polarizable ligands.

EXPERIMENTAL

Materials

Dry sulfur dioxide (Baker) was further dried through a column containing $P_4O_{10} + CaCl_2$. Dichloromethane was dried over $CaCl_2$ and distilled. All other solvents were of reagent grade and were used without further purification. The complexes $[Rh(CO)_2(Piperidine)Cl]$, $[C_8H_{12}RhCl(PPh_3)]$[16], $[C_8H_{12}RhCl(Piperidine)]$[16], $[(C_7H_8)RhCl(PPh_3)]$[11], $[(CO)_2RhCl]_2$[17,18], *trans*-$[(CO)_2RhCl(PPh_3)]$[19], $[(C_8H_{12})IrCl(PPh_3)]$[20] were prepared according to the literature.

SO_2-adducts

$[(C_8H_{12})RhCl(PPh_3)(SO_2)]$. The yellow $[(C_8H_{12})RhCl(PPh_3)]$ in dichloromethane was treated with a steady stream of SO_2, reaction took place within a few

TABLE 1

DESORPTION TEMPERATURES AND INFRARED ABSORPTIONS OF SULFUR DIOXIDE IRIDIUM AND RHODIUM COMPLEXES[a]

Complex	Desorption temp. of SO_2 (°C)	SO stretch (Nujol) (cm^{-1})	Ref.
$[C_8H_{12}RhCl(PPh_3)(SO_2)]$	80	1218, 1050	This work
$[C_7H_8RhCl(PPh_3)(SO_2)]$	130	1215, 1050	This work
$[C_8H_{12}RhCl(Pip)(SO_2)]$	220 dec.	1200, 1050 (broad bands)	This work
$[RhCl(SO_2)(CO)_2(PPh_3)]$[b]		1215, 1057	This work
$[RhCl(SO_2)(CO)(PPh_3)_2]$		1214, 1188, 1057	1
$[RhCl(SO_2)(CO)_2(Pip)]$	150	1200, 1050 (broad bands)	This work
$[IrCl(SO_2)(CO)(PPh_3)_2]$	150	1198, 1185, 1048	1
$[Ir(C_8H_{12})Cl(SO_2)(PPh_3)]$	145	1200, 1050	This work

[a] The increase of ν(CO) in the adducts points to an increase of oxidation state of the metal caused by "oxidation addition" of SO_2[1]. [b] ν(CO) at 2040 cm^{-1}.

min at room temperature to give a red solution. Evaporation of the solvent in a stream of SO_2 left an air-stable red solid the IR spectrum of which showed two strong bands at 1050 and 1218 cm^{-1}. The adduct was stable enough to be isolated and characterized by elemental analyses. The same reaction was carried out in heterogeneous conditions by passing a stream of SO_2 gas over solid $[(C_8H_{12})RhCl(PPh_3)]$ placed on fritted glass at −7°. The rate of the reaction depends markedly on the temperature, being instantaneous at −7° and exceedingly slow at 50°. The SO_2 uptake can be reversed, as shown by the color change that is observed when the adduct in the solid state is alternately heated (red→yellow at >80°) and cooled in a SO_2 atmosphere (yellow→red). The yellow solid that is obtained upon heating the SO_2 adduct has a melting point and IR spectrum identical with the starting complex $[(C_8H_{12})RhCl(PPh_3)]$ even after several heating–cooling cycles. The complex is quite labile in solution, its red color persisting only in solvents saturated with SO_2. From its yellow solutions in benzene, ethyl ether, hexane, dichloromethane chloroform $[(C_8H_{12})RhCl(PPh_2)]$ slowly crystallizes out.

$[(C_7H_8)RhCl(PPh_3)(SO_2)]$. This was prepared in the same way as the above. It is a red solid having IR bands at 1050 and 1215 cm^{-1}. This compound loses SO_2 at a slightly higher temperature than that described above (ca. 130°). It also gives yellow solutions in SO_2-free solvents with eventual forming of the original tetracoordinate complex.

$[(C_8H_{12})RhCl(Piperidine)(SO_2)]$. $[(C_8H_{12})RhCl(Piperidine)]$ in the minimum amount of toluene was treated with a stream of SO_2. The solution turned red in few minutes and the precipitated red solid was filtered off and washed with hexane. The IR spectrum of this compound is not easy to interprete since it shows very broad bands. Sulfur dioxide is firmly bound to the metal. The complex does not give the starting material upon heating, but decomposes at ca. 220°, whereas its parent derivative, $[(C_8H_{12})RhCl(Piperidine)]$, decomposes in the range 150–170°. It is insoluble in most solvents except chloroform, in which it gives yellow solutions.

$[(CO)_2RhCl(PPh_3)(SO_2)]$. The SO_2 uptake was very slow in both homogeneous and heterogeneous phases. Owing to the lability of the metal–SO_2 bond it was not possible to isolate the adduct, which was identified only by its IR spectrum. When the yellow *trans*-$[(CO)_2RhCl(PPh_3)]$ was kept for ca. 20 days in SO_2 atmosphere, a slight change in color towards red was noticed. The IR spectrum in the carbonyl stretching region indicated the presence of a mixture of the starting complex and of a compound having a higher $\nu(CO)$ (2030 cm^{-1}); the characteristic bands of SO_2 coordinated were at 1052 and 1210 cm^{-1}.

$[(CO)_2RhCl(Piperidine)(SO_2)]$. This was prepared as above, both in dichloromethane solution and under heterogeneous conditions. In this latter case the reaction took place immediately at −7°. Like the analogous cyclooctadiene adduct, this compound has a complicated IR spectrum with very broad bands. It loses SO_2 at ca. 160° and is unstable in SO_2-free solvents in which it gives yellow solutions.

$[(C_8H_{12})IrCl(PPh_3)SO_2]$. $[(C_8H_{12})IrCl(PPh_3)]$ treated with SO_2 in dichloromethane solution or in the solid at room temperature gave almost instantly a red solid, the IR spectrum of which show the bands of coordinated SO_2 at 1050 and 1200 cm^{-1} (m.p. 142–145°).

SO_2-absorption measurements

To determine the stoichiometry of these adducts, gas absorption measurements were carried out at 20°. The apparatus employed was a modification of that used by Bolland[21] and gave direct readings of volumes of absorbed SO_2 at constant pressure. In order to avoid large errors caused by the extreme solubility of SO_2 in all solvents available, the absorption measurements were carried out directly on the solid $[(C_8H_{12})RhCl(PPh_3)]$. The reproducibility was not always satisfactory owing to the varying crystal size of samples employed. Long absorption times were used to allow the reactions to go to completion. The absorbed SO_2/complex molar ratios varied in the range 1.2–1.3, indicating that the resulting product is a 1/1 adduct. The slight excess of absorbed SO_2 is probably due to gas molecules trapped by the solid.

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