Journal of Organometallic Cgemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Solid state reversible reactions of square planar d^8 complexes with sulfur dioxide

ENEO C. MORONI, R.A. FRIEDEL and IRVING WENDER
Pittsburgh Coal Research Center, U.S. Bureau of Mines, Pittsburgh, Pa. 15213 (U.S.A.)

(Received October 23rd, 1969)

A study was initiated on the possibility of employing organometallics in the solid state to remove SO_2 from flue gases. The reversible reaction of SO_2 with transition metal complexes has been the subject of recent investigations[1-4]. These reactions were carried out in solution and the SO_2 adducts readily separated in crystalline form[1,2].

We observed that at ambient temperature and atmospheric pressure the crystals of *trans*-$IrCl(CO)(PPh_3)_2$ (I) also react reversibly with gaseous SO_2, and rapidly pick up more than one mole of SO_2 per mole. Molecular oxygen also forms a 1/1 adduct with I in benzene solution but does not react with crystals[5] of I. Both O_2 and SO_2 are present in flue gases and the selective sorption of SO_2 by the crystals of I was viewed as an additional benefit provided by the reaction in the solid state*.

RESULTS

Crystals of square planar complexes of the types $MX(CO)(PPh_3)_2$ and $[M(P{-}P)_2]^+X^-$ where M = Ir and Rh; X = Cl, Br, and I; $PPh_3 = P(C_6H_5)_3$ and P–P = $[(C_6H_5)_2P{-}CH_2]_2$ ("diphos") react rapidly with gaseous SO_2 at ambient temperature and atmospheric pressure. The reactions are exothermic** and are markedly affected by the temperature and the partial pressure of SO_2. The solid state reactions are reversible as are those carried out in solution and their sorption–desorption equilibrium data are shown in Table 1.

As expected, SO_2 uptake decreases, while the rate of SO_2 sorption increases with increasing temperature. At 25°, SO_2 uptake is rapid in the first 10 min and equilibrium is usually reached in less than 40 min.

No significant effect of crystal size on yield, rate or exothermicity of SO_2 sorption was observed, an indication that very little SO_2 is physically adsorbed.

---

*Apparatus for sorption and desorption of gases from solids was modified to determine the amount of gas precisely both by weight and by volume and for an indefinite number of sorption and desorption cycles.

**Temperature of the crystal bed increases rapidly within 3–4 min. With 1 mmole (1.115 g) of the most reactive complex, $[Ir(P{-}P)_2]^+I^-$, the reaction temperature reaches 47° (reactor immersed in thermostatic bath at 25 ± 0.2°).

Total desorption of SO_2 by heating is possible only with $RhCl(CO)(PPh_3)_2$, whereas an inert gas sweep or pumping is needed in addition to heating, to remove practically all the SO_2 from the other complexes. A more accurate account of the desorption of SO_2 from the adduct $IrCl(CO)(PPh_3)_2 \cdot 1.8\ SO_2$ was determined by monitoring the reaction by mass spectrometry.

TABLE 1

SO_2 PICKUP BY TRANSITION METAL COMPLEXES AT EQUILIBRIUM
moles SO_2/mole complex in SO_2 atmosphere (740 mm Hg) at various temperatures

Complex	-5°	0°	25°	45°	90°	120°	180°	Argon sweep 180°C
$IrCl(CO)(PPh_3)_2$	1.89	1.89	1.82	1.60	0.87	0.51	0.42	0.30
$IrBr(CO)(PPh_3)_2$	1.99	1.87	1.75	1.73	1.11	1.08	0.11	0.02
$IrI(CO)(PPh_3)_2$	2.30	2.29	1.98	1.94	1.60	1.21	0.51	0.22
$RhCl(CO)(PPh_3)_2$	0.81	0.81	0.81	0.75	0.75	0.00	–	–
$Ir(P{-}P)_2Cl$	5.84	4.93	3.67	3.33	3.08	2.84	1.75	0.41
$Ir(P{-}P)_2Br$	7.75	6.69	4.32	2.90	2.71	2.32	1.13	0.41
$Ir(P{-}P)_2I$	8.08	7.62	4.62	3.37	2.31	1.79	0.52	0.19
$Rh(P{-}P)_2Cl$	3.98	3.89	3.05	3.02	2.95	2.60	1.90	0.27

Desorption curves for this compound revealed two maxima at 65 ± 3° and at 120 ± 5° which are evidence for two differently bonded SO_2 adducts. Up to 180° no other species except SO_2 are eliminated from the iridium complex and decomposition products, mainly benzene and CO_2, are evident above 180°.

Several cycles of SO_2 sorption and desorption were carried out and results show that the reversible reaction is reproducible.

INFRARED SPECTRA

The carbonyl stretching frequencies of $MX(CO)(PPh_3)_2$ complexes and their SO_2 adducts reveal that addition of SO_2 shifts the $\nu(CO)$ to higher frequencies. The extent of the shifts are the same as those obtained for the 1/1 SO_2 adducts crystallized from solutions[1,2] which indicates that only one mole of SO_2 is bonded to the central metal in the solid complex. In addition to absorption bands corresponding to vibrational frequencies of coordinated SO_2, which are similar to those of the 1/1 SO_2 adducts prepared from solutions, new bands appear in the same regions of the symmetric and asymmetric stretching and bending frequencies of SO_2[★]. These were arbitrarily assigned to the additional moles of SO_2 which are not coordinated to the metal, but evidently are somewhat bonded or "associated" (as differentiated from coordinated) to the complexes. The assignment of and distinction between bands of coordinated and associated SO_2 were done

---

[★] KBr pellets or Nujol mull preparation of the SO_2 adducts causes loss of the additional SO_2. A method was devised to allow the addition of SO_2 to the complexes *in situ*. The parent complexes, compressed in KBr, pick up SO_2 to the same extent as the free crystals, whereas KBr alone does not: a clean-cut solid state reaction occurs within the pellet, without loss of SO_2.

on the basis of observed reduction of maximum area of the associated SO_2 band upon inert gas sweep, eventually combined with gradual heating. The bands of the coordinated SO_2 are not reduced by these mild conditions.

The vibrational frequencies of the asymmetric stretching of both coordinated (ν_3) and associated (ν_3^a) SO_2 are represented by very strong bands, whereas those of the symmetric stretching and bending are in some cases very weak; therefore, only the ν_3 and ν_3^a values were listed in Table 2 for comparison.

TABLE 2

VIBRATIONAL FREQUENCIES (cm^{-1}) OF "COORDINATED" AND "ASSOCIATED[a]" SO_2

Parent compound	Asymmetric stretching	
	ν_3	ν_3^a
$IrCl(CO)(PPh_3)_2$	1198, 1180	1325
$IrBr(CO)(PPh_3)_2$	1200, 1189	1325
$IrI(CO)(PPh_3)_2$	1202, 1189	1321
$RhCl(CO)(PPh_3)_2$	1210, 1180	1324
$[Ir(P{-}P)_2]Cl$	1285, 1154	1285
$[Ir(P{-}P)_2]Br$	1288, 1152	1288
$[Ir(P{-}P)_2]I$	1268, 1156	1268
$[Rh(P{-}P)_2]Cl$	1288, 1172	1302
SO_2 gas	— —	1362
SO_2 solid[7]	— —	1330, 1308
$(C_6H_5)_4SbBr$	1288	1301
$(CH_3)_4NBr$	—	1302

It was thought that SO_2 would react with certain ionic compounds to give adducts[6a,b] in which the SO_2 would be bonded to the compound as the additional SO_2 is bonded to the square planar d^8 complexes. Of the compounds investigated only two, $(C_6H_5)_4SbBr$ and $(CH_3)_4NBr$, reacted in the solid state with one or more moles of SO_2 per mole; the assigned vibrational frequencies of the associated SO_2 are also listed in Table 2, together with those of free SO_2 gas and solid. The bands representing the vibrational frequencies of SO_2 bonded to $(C_6H_5)_4SbBr$ and $(CH_3)_4NBr$ are well defined and are very close to those of solid SO_2, rather than those of SO_2 gas, as expected. They are easily reduced upon inert gas sweeping. They are also located in the same region as the bands assigned to ν_3^a of most of the square planar d^8 complexes*. The exception is provided by the Ir-diphos complexes whose ν_3 and ν_3^a are represented by a broad single band in which ν_3^a is shifted downward to overlap with ν_3. The fact that the Ir-diphos complexes react with substantially more moles of SO_2 and hold at least part of them more tightly (Table 1), would explain the ν_3^a downward shift and the much broader band area. Furthermore, part of the broad band decreases upon inert gas sweeping and this part should correspond to the ν_3^a of the Ir diphos complexes by similarity of behavior with the ν_3^a's of the Rh-diphos and those of $MX(CO)(PPh_3)_2$ complexes which are readily distinguished from their ν_3's.

---

*This holds true for the symmetric stretching ν_1^a and bending ν_2^a vibrational frequencies.

Solid state reaction of the SO_2 adduct of I with O_2 and that of the O_2 adduct of I with SO_2 did not produce the sulfate adduct as in some platinum complexes[8]. This is in agreement with the observed reproducibility of the sorption–desorption cycles.

DISCUSSION

For $MX(CO)(PPh_3)_2$ complexes the bonding of one mole of SO_2 to metal is demonstrated by the $\Delta\nu(CO)$ and by the vibrational frequencies of the coordinated SO_2. The latter are present also in the diphos complexes, thus attesting that similar bonding occurs for these complexes. For additional SO_2 there was no evidence of SO_2 bonding to any of the ligands.

Uptake of non-coordinatively bonded SO_2 is especially large in the case of the diphos ionic complexes. Results of a study of SO_2 uptake of several ionic compounds not containing transition metals are shown in Table 3. The uptake seems to be related to the difference in size and electrical charges of the cation–anion system or, in other words, to the dipole moment of the complex. In fact, SO_2 uptake increases in going from Cl to I with the diphos complexes; for somewhat smaller cations such as $(C_4H_9)_4N^+$ and $(C_7H_{15})_4N^+$ there is maximum uptake at the Br derivatives. For the small $(CH_3)_4N^+$, a dramatic decrease of SO_2 uptake occurs on going to the larger anion.

TABLE 3

GASEOUS SO_2 UPTAKE BY IONIC COMPOUNDS AT EQUILIBRIUM

Moles SO_2/mole compound in SO_2 atmosphere (740 ± 5 mm Hg) at 25 ± 0.5°

Anions	Cations			
	$(CH_3)_4N$-	$(C_4H_9)_4N$-	$(C_7H_{15})_4N$-	Ir[P–P]$_2$-
-Cl	2.82	2.93	3.38	3.67
-Br	1.01	3.49	3.52	4.48
-I	0.00	3.39	3.42	4.86

The uptake of SO_2 by $MX(CO)(PPh_3)_2$ complexes varies similarly with halogen size and electronegativity; perhaps, the additional SO_2 is bonded to the metal–halogen system in which the dipole moment $M^{\delta+}$–$X^{\delta-}$ is enhanced by the introduction of the SO_2 coordinated to the metal.

The type of bond here described for the additional SO_2 seems to be of the same nature as the solvation bond, *e.g.*, between liquid SO_2 and polar compounds[6a,b]. More work is needed to establish the nature of this bond.

ACKNOWLEDGEMENTS

We are grateful for the useful suggestions given us by Professor L. Vaska and Dr. H.W. Sternberg.

REFERENCES

1 L. Vaska and S.S. Bath, *J. Amer. Chem. Soc.*, 88 (1966) 1333.
2 L. Vaska and D.L. Catone, *ibid*, 88 (1966) 5324.

3 L.H. Vogt, Jr., J.L. Katz and S.E. Wiberly, *Inorg. Chem.*, 4 (1965) 1157.
4 S.J. LaPlaca and J.A. Ibers, *Inorg. Chem.*, 5 (1966) 405.
5 L. Vaska, *Science*, 140 (1963) 809.
6a N.N. Lichtin, *Progress in Physical Organic Chemistry*, Vol. 1, Wiley, New York, 1963, p. 75–108.
6b T.C. Waddington, in T.C. Waddington (Ed.), *Non-Aqueous Solvents*, Academic Press, New York, 1965, p. 253–284.
7 R.N. Wilson and E.R. Nixon, *J. Chem. Phys.*, 25 (1956) 175.
8 C.D. Cook and G.S. Jauhal, *J. Amer. Chem. Soc.*, 89 (1967) 3066.