# The Addition of Oxygen to Carbonyl Groups: the Reactivity of Bistriphenylphosphineplatinum(0)–Oxygen

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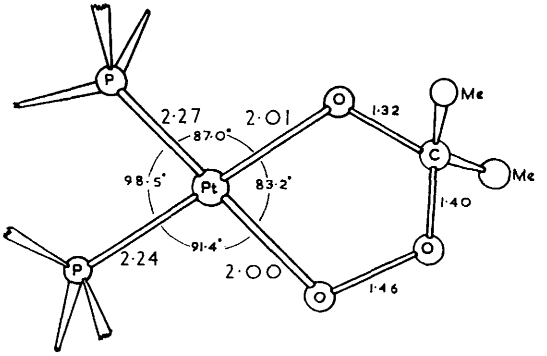
THE high reactivity of the co-ordinated oxygen molecule in bistriphenylphosphineplatinum(0)–oxygen is, for example, illustrated by the formation of carbonato- and sulphato-complexes from carbon dioxide and sulphur dioxide respectively.[1] We now describe a novel addition of the oxygen to carbonyl groups in a variety of organic substrates.

Recrystallisation of the oxygen complex from acetone provides very pale yellow crystals which are monoclinic with $a = 9{\cdot}83$, $b = 9{\cdot}06$, $c = 37{\cdot}90$ Å, $\beta = 95{\cdot}6^\circ$; $Z = 4$; space group $P2_1/c$. *X*-Ray reflexion intensities were measured on a Pailred diffractometer (Cu-$K_\alpha$ radiation) and 2342 non-equivalent reflexions were judged of significant value $(F^2{}_{\mathrm{O}}/\sigma F^2{}_{\mathrm{O}}) \geqslant 3{\cdot}0$). Of these reflexions only 1735, having $F^2{}_{\mathrm{O}}/\sigma(F^2{}_{\mathrm{O}}) \geqslant 10{\cdot}0$, have been used in the initial structural determination and refinement (to *R* 0·058: further refinement, using all of the observed data, corrected for absorption effects, is underway). The molecular geometry is shown in the Figure; estimated standard deviations in the bond-lengths average Pt–P 0·01, Pt–O 0·01, O–O, C–O and C–C 0·04 Å The structure is seen to correspond to the addition of oxygen to the carbonyl group with the formation of a ketone–peroxy-chelate ring. The chelate ring is not completely planar (r.m.s. deviation 0·12 Å) but the co-ordination geometry around the platinum atom is close to planar (r.m.s. 0·04 Å). The bond-lengths are quite normal, at least within the stated error limits.

In solution ($CDCl_3$) the $^1$H n.m.r- spectrum consists of a singlet, $\tau = 8{\cdot}45$ (7·91 in acetone itself) with a ratio of 1 : 5 to the hydrogens of the triphenylphosphine ligands. The i.r. spectrum shows no $\nu_{C=O}$ or $\nu_{O\text{-}O}$ stretching frequencies; the very strong bonds at 1290 and 975 cm$^{-1}$ can be assigned to $\nu_{C\text{-}O}$ stretching vibrations while a weaker one at 855 cm.$^{-1}$ may probably be assigned to $\delta_{C\text{-}O}$.



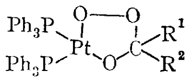
FIGURE

It has been suggested,[2] on the basis of the bond-lengths in a number of iridium(I)–oxygen complexes,[3] that the electron distribution in molecular oxygen, "$\pi$-bonded" to a transition-metal ion in a low oxidation state, approximates to a varying extent that of the $^3\Sigma_u^-$ excited state. This suggestion seems particularly relevant to considerations of the reactivity of the co-ordinated oxygen. In valence-bond terms, the $^3\Sigma_u^+$ excited state of oxygen is largely a covalent structure dissociating into neutral atoms; the $^3\Sigma_u^-$ state is mainly the ionic structure, $O^+–O^-$. Thus a conventional nucleophilic addition to the carbonyl group can easily be envisaged.

We have also investigated the reactions of $(Ph_3P)_2PtO_2$ with, for example, acetyldehyde, methyl ethyl ketone and benzaldehyde. The n.m.r. data ($\tau$ values) of these complexes are summarised below.

The relative reactivity of these organic substrates is qualitatively related to the polarity of the carbonyl bond. Amides and esters do not react with the phosphineplatinum–oxygen adduct while acetaldehyde reacts more rapidly than acetone. The present results have some implications to views on the mechanisms of heterogeneous catalytic oxidation.

TABLE



| $R^1$ | $R^2$ | $^1H$ n.m.r. spectra |
|---|---|---|
| Me | Et | 8·25[2] q, 9·25[3] t; *J* 7·5 c./sec. 8·50[3] s |
| H | Me | 4·82[1] (br, q), 8·62[3], asymmetric quintet; *J* 4·9 c./sec. |
| H | Ph | 4·07 br, s. |

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[2] R. Mason, *Nature*, 1968, **217**, 543.

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