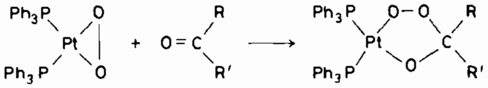
Kinetics and Mechanisms of Inorganic Reactions

Solvent Effects on the Kinetics of the Insertion of Ketones into the Dioxygen Adduct $Pt(PPh_3)_2O_2$

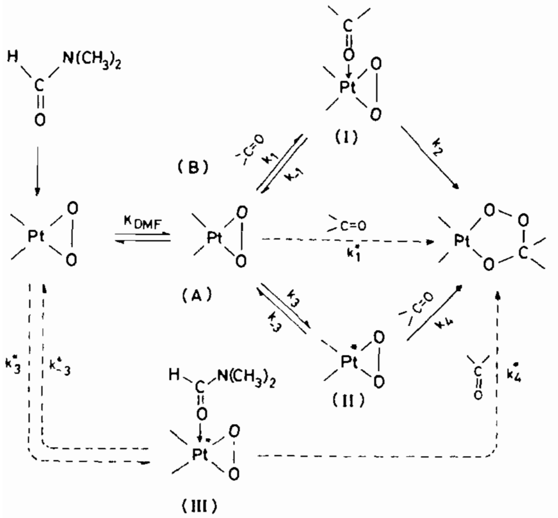
A. FUSI, G.-M. ZANDERIGHI and R. UGO

Istituto di Chimica Generale ed Inorganica, Centro C.N.R., Via Venezian 21, 20133 Milan, Italy

The insertion reaction into $Pt(PPh_3)_2O_2$ of an unsaturated group such as the double bond of activated olefins or the carbonyl group of some organic molecules can be considered to be a model for some of the important steps of catalytic selective oxidations [1, 2]. We report here the results of a kinetic investigation on the reaction:



The experimental rate law is in agreement with a dual pathway reaction mechanism (see scheme)

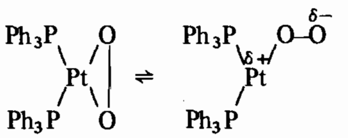


Ketones:
a) Acetone; b) 1,1,1-Trifluoroacetone; c) Methylisobutylketone; d) Methylethylketone; e) Cyclobutanone; f) Cyclopentanone; g) Cyclohexanone; h) Cyclopentanone.

Solvents:
1) Benzene; 2) Acetonitrile; 3) THF; 4) 1,2-Dichloroethane; 5) Chloroform; 6) Propylene carbonate; 7) DMF; 8) Methanol.

The major path (B) involves precoordination of the ketone to the vacant axial coordination site of platinum (intermediate I) followed by an insertion of the carbonyl group into the PtO_2 moiety. The order of reactivity found is b >>> a > c > d and e > g > f > h. In this path a trend corresponding to a linear decrease in the reaction rate with increasing solvent polarity was observed.

The parallel path (A) involves the slow formation of an activated form of the dioxygen complex (species II) which reacts rapidly with the ketone. The overall rate decreases in the presence of a polar aprotic solvent and this effect is more pronounced in path (A). As a matter of fact the rather negative $\Delta S^{\neq}$ values found suggest a strong solvation of both intermediates I and II not only by means of dipolar interactions but also by coordinatively saturating the metal center. Moreover the overall rate increases markedly in the presence of methanol. This appears to be a consequence of the presence of hydrogen bonding between the solvent and the coordinated peroxide ligand in the intermediates I and II. Again this effect is more important in path (A). For this latter the higher $\Delta H^{\neq}$ values found are in agreement with the large energy required to break a Pt–O bond in order to generate an end-on bonded structure such as:



We suggest that this particular 1,3 dipolar form for the O_2 ligand can react even with relatively weak electrophiles such as ketones.

References

1 P. A. Kilty and W. M. H. Sachtler, *Catalysis Rev.*, *10*, 1 (1974).
2 H. Mimoun, M. Perez Machirant and I. Serée de Roch, *J. Am. Chem. Soc.*, *100*, 543 (1978), and references therein.