Reversible Oxygenation of Metal Complexes: Electronic and Steric Factors

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Summary The rates of oxygen addition to *trans*-$[IrCl(CO)(R_3P)_2]$ (R_3P = tertiary phosphine) and the stability of the resulting dioxygen adducts, $[O_2IrCl(CO)(R_3P)_2]$, increase with increasing basicity of the substituent R, provided the substituents have comparable structures; the geometry of R exerts a profound effect on the dynamics of these reactions.

WE report some results of a kinetic study of the reversible reactions of molecular oxygen with a series of iridium complexes (equations 1, 2) which offer a new insight into (a) the role of the ligands in the oxygen-carrying compounds and (b) the mechanism of these reactions.

$$[IrCl(CO)L_2] + O_2 \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} [O_2IrCl(CO)L_2] \qquad (1)$$

L = tertiary phosphine or arsine; k_2 = second-order rate constant; k_{-1} = first-order rate constant (see Table).

$$K_2 = k_2/k_{-1} = [O_2IrCl(CO)L_2]/[IrCl(CO)L_2][O_2] \qquad (2)$$

The data in the Table are given in the order of increasing rates of oxygenation (k_2) which is nearly the same as the sequence of the stability constants for the dioxygen adducts (K_2). At first glance, these results do not seem to display an obvious correlation with the electronic properties of L (*e.g.*, basicity, ν_{CO}). However, if one compares a group of complexes in which the ligands are isostructrual or nearly so, (**2**), (**3**), (**6**) and (**9**), it is found that log k_2 (or ΔH_2^*) is inversely proportional to the Hammett σ constant for the *para*-substituent in the arylphosphine ligand $(p\text{-}XC_6H_4)_3P$ (equation 3), or directly proportional to the basicity of the tertiary phosphine.

$$\log k_2 = 0{\cdot}194 - 14{\cdot}1\,\sigma\,(X) \qquad (3)$$

$$(k_2, \text{Table};\ X = Cl,\ H,\ CH_3,\ CH_3O)$$

A correlation related to that in equation 3 is found also between the dynamic constants (k_2 or K_2) and the carbonyl stretching frequency (ν_{CO}) in the four parent complexes, *i.e.*, basicity ($1/\nu_{CO}$): (**9**) > (**6**) ≈ (**3**) > (**2**) (Table). According to this observation, and the usual interpretation that the ν_{CO} reflects a relative "latent basicity" of a carbonyl complex, one would expect compound (**1**) to exhibit the

TABLE

Kinetic, stability and activation paramaters[a] *for the reversible reactions of molecular oxygen with* trans-[IrCl(CO)L_2] (*see eqs.* 1, 2) *in chlorobenzene*[b] *at* 40°

No.	L	ν_{CO}[c] cm^{-1}	$10^2 k_2$ M^{-1} s^{-1}	$10^6 k_{-1}$ s^{-1}	$10^{-3} K_2$ M^{-1}	ΔH_2^* kcal mol^{-1}	ΔS_2^* e.u.
(**1**)	$(C_6H_{11})_3P$	1934	0·127	5·85	0·217	9·5	−42
(**2**)	$(p\text{-}ClC_6H_4)_3P$	1966	3·10	8·67	3·58	10·8	−31
(**3**)	$(C_6H_5)_3P$	1956	9·93	13·9	7·14	9·5	−33
(**4**)	$(C_6H_5)_3As$	1946	14·2	8·25	17·2	8·1	−37
(**5**)	$(C_6H_5)_2(C_2H_5)P$	1949	14·2	6·75	21·0	8·4	−36
(**6**)	$(p\text{-}CH_3C_6H_4)_3P$	1956	21·6	12·2	17·7	9·3	−32
(**7**)	$(n\text{-}C_4H_9)_3P$	1937[d]	26·1	3·90	66·9	9·0	−33
(**8**)	$(C_2H_5)_3P$	1948	33·8	1·57	215	8·5	−34
(**9**)	$(p\text{-}CH_3OC_6H_4)_3P$	1947	48·4	12·5	38·7	8·5	−33

[a] The rate data were obtained by monitoring the intensity of an absorption band (377—387 nm) in the electronic spectrum of [IrCl(CO)L_2]. The activation parameters have been calculated from the kinetic constants (k_2) determined at different temperatures (20—60°). Subscript 2 refers to the second-order oxygenation reaction, subscript −1 to the first-order deoxygenation reaction. Maximum standard deviations: $k_2 \pm 1$; k_{-1}, ±4; K_2, ±2%; ΔH_2^*, ±0·5 kcal mol^{-1}; ΔS_2^*, ±3 e.u.

[b] *Ca.* 10^{-4}M in metal complex; $p(O_2)$: 500—750 mm, oxygenation (O_2: Ir = 10—60); ~0 mm deoxygenation.

[c] In *trans*-[IrCl(CO)L_2], measured in Nujol.

[d] Measured in chlorobenzene.

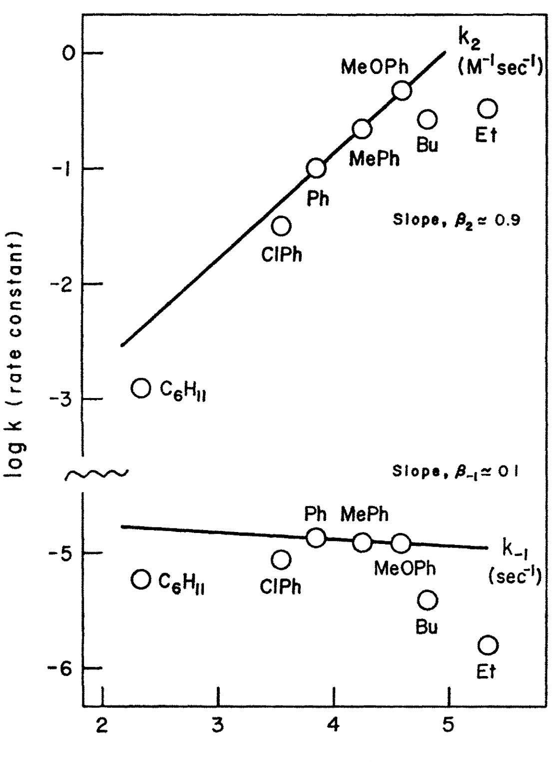

FIGURE. *Linear free energy relationships (LFER) for the reversible oxygenation of* [IrCl(CO)$(R_3P)_2$] [*equations* (1,2)] *in chlorobenzene at* 40°. R_3P : C_6H_{11} = $(C_6H_{11})_3P$; ClPh = $(p\text{-}ClC_6H_4)_3P$; Ph = $(C_6H_5)_3P$; MePh = $(p\text{-}CH_3C_6H_4)_3P$; MeOPh = $(p\text{-}CH_3OC_6H_4)_3P$; Bu = $(n\text{-}C_4H_9)_3P$; Et = $(C_2H_5)_3P$.

highest affinity for O_2 among the derivatives given in the Table. In fact, however, the tricyclohexylphosphine complex (**1**) is least reactive (k_2) and forms the weakest dioxygen adduct (K_2). This apparent discrepancy finds an explanation in the linear free energy relationships (LFER) depicted in the Figure. As expected, the reactions of the three triarylphosphine complexes display a single mechanism,† but the marked deviation of the data for (**1**) and the other trialkylphosphine complexes from the two reference lines shows that these reactions involve different mechanistic details which presumably are of steric origin.[1] Two further examples demonstrate a distinction between the electronic and steric factors influencing reactivity: when L (equation 1, Table) is $(C_6F_5)_3P$ (ν_{CO}, 1994 cm^{-1}) or $(o\text{-}CH_3C_6H_4)_3P$(ν_{CO}, 1946 cm^{-1}), *no reaction* with oxygen is observed (footnote *b*, Table). The inactivity of the former can be attributed largely to a lack of required electron density on the metal (*cf.* ν_{CO}), but the inertness of the latter must be solely due to a geometric effect (*ortho*-CH_3) which overrides the favourable electronic disposition (basicity, ν_{CO}).

The value of the slope (β_2 or β_{-1})[2] in the Figure implies that the configuration of the transition state of the reversible oxygenation (equation 1) of the three triarylphosphine complexes closely resembles that of the dioxygen adducts.[3] The similarity between the activation ($\Delta S_2^* \approx -33 \pm 2$ e.u.) and overall ($\Delta S_2^0 \approx -31 \pm 4$ e.u.) entropies for these oxygenation reactions supports the same premise.

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† The lines in the Figure have been arbitrarily drawn through the three points representing structurally similar complexes; the points for L = Ph_3As and Ph_2EtP have been omitted for clarity since they fall close to those of $(p\text{-}CH_3C_6H_4)_3P$.

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[3] L. Vaska, *Accounts Chem. Res.*, 1968, **1**, 335; S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, 1964, **87**, 2581.