Homogeneous Catalytic Activation of O–H and N–H Bonds in Organic Molecules by Ruthenium, Osmium, Rhodium, and Iridium Complexes

By G. G. Eberhardt
(*Sun Oil Company, Marcus Hook, Pennsylvania* 19061)
and Maher E. Tadros and L. Vaska*
(*Department of Chemistry, Clarkson College of Technology, Potsdam, New York* 13676)

Summary H–D isotopic exchange between D_2 and CH_3COOH, CH_3OH, C_2H_5OH or morpholine is observed in the presence of some Ru^{II}, Os^{II}, Rh^{I} or Ir^{I} complexes at ambient conditions; analogous compounds of $Pt^{0,II}$, $Pd^{0,II}$, Ni^{II}, Co^{II} and Fe^{II} are inactive.

We have examined a number of tertiary phosphine complexes of group VIII metals for their ability to catalyse the isotopic exchange reactions given in equation (1). The results provide some significant information on the factors influencing these new homogeneous catalyses and reveal an apparently unusual pattern for kinetic isotopic distribution (Figure).

$$RH + D_2 \xrightarrow{\text{Catalyst}} RD + HD, H_2 \qquad (1)$$

RH = organic molecule, see Table.

The exploratory data summarized in the Table show the relative catalytic activities of some Ru, Os, Rh, and Ir complexes and compare the extent of the exchange as a function of the organic substrate. The relative rates of the catalyses are evident from the percentage unreacted D_2 (Table, footnote b). The following complexes were found to exhibit no significant catalytic activity for any of the four reactions (see equation 1, and Table footnote c): $[FeCl_2L_2]$, $[CoCl_2L_2]$, $[RhCl(CO)L_2]$, $[Rh(L–L)_2]Cl$, $[NiCl_2L_2]$, $[PdCl_2L_2]$, $[PdL_4]$, $[PtCl_2L_2]$, and $[PtL_4]$; L = Ph_3P, L–L = $Ph_2PCH_2CH_2PPh_2$.

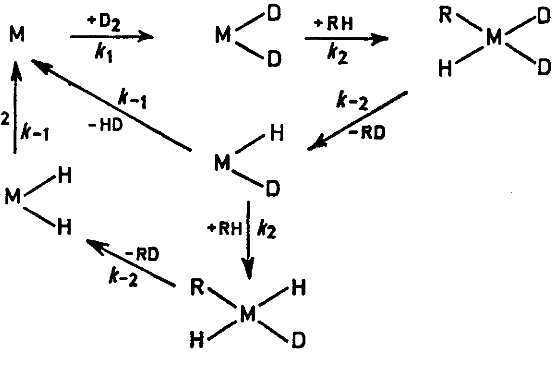
Table

Hydrogen-deuterium exchange between D_2 *and some organic solvents* (RH, *equation* 1) *catalysed by metal complexes in solution at* 22° [a,b]

		CH_3COOH		CH_3OH		C_2H_5OH		OC_4H_8NH[d]	
No.	Complex[e]	HD (%)	H_2 (%)	HD (%)	H_2 (%)	HD (%)	H_2 (%)	HD (%)	H_2 (%)
(1)	$[RuCl_2L_3]$	3	94	6	88	43	41	25	7
(2)	$[OsBr_2L_3]$[f]	1	98	45	26	36	11	10	9
(3)	$[RhClL_3]$	16	47	45	39	44	20	25	8
(4)	$[IrH_2ClL_3]$[f]	22	68	1	68	1	18	14	38
(5)	$[IrH_3L_3]$	8	47	N.E.[c]		N.E.[c]		N.E.[c]	
(6)	$[IrCl(CO)L_2]$[f,g]	10	72	42	24	N.E.[c]		5	7

[a] $2 \cdot 0 \times 10^{-5}$ mol of the complex in 30 ml of the solvent (previously dried over molecular sieves and degassed) under atmospheric pressure of D_2(p_T, 800 mm). Initial mol ratios, complex : D_2 : solvent = 1 : 140 : > 10^4. [b] Percentages of HD and H_2 were analysed (by mass spectrometry) after 3 h experiments unless noted otherwise, see footnotes d and g. Balance is D_2, *i.e.*, $\%D_2 = 100 - \%HD - \%H_2$. Because of the high initial hydrogen (solvent)-deuterium (D_2) ratio, the gas phase at equilibrium is expected to consist of only small percentages of D_2 and HD and nearly 100% of H_2. Composition of the D_2 used: D_2, 95; HD, 1·1; H_2, 3·9%. [c] N.E. = no significant exchange observed during the time indicated. The results were considered to be negative when only a few percent HD and/or H_2 above the initial values were detected. This could be attributed to the exchange between D_2 and *ortho* hydrogens of the phenyl groups of Ph_3P.[1] [d] Morpholine; reaction time, 16 h. [e] L = Ph_3P. [f] 20 ml of toluene added to effect dissolution. [g] Reaction times: for experiments with CH_3COOH, 6 h; for other experiments, 16 h.

It is seen (Table) that (i) there is a general decrease in the the reaction rates with decreasing acidity of the exchangeable hydrogen bonded to O or N, *i.e.*, $CH_3CO_2H > CH_3OH > C_2H_5OH > OC_4H_8NH$. (ii) The catalytic activity is, as expected, strongly dependent on the identity of the metal atom (position in the periodic table, oxidation state, d^n configuration) and the nature of the ligands, evident from both the positive (Table) and negative (see above) results.



R = $MeCO_2$, MeO, C_2H_5O or OC_4H_8N

Scheme†

The results of some of the reactions show an apparently peculiar isotopic distribution (Table): in the *incomplete* catalyses, **(4)** + MeOH, EtOH and **(5)** + $MeCO_2H$, only small fractions of HD are observed. A detailed kinetic study of the latter system confirmed the low concentration of HD even in the very initial stages of the reaction. This is depicted in the Figure which also includes "normal" or typical rate curves {$[RuCl_2(Ph_3P)_3]$ **(1)**} expected under these conditions, *i.e.*, an initial production of HD which

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† The given sequence of the two initial steps is arbitrary; the kinetic and thermodynamic isotope effects are neglected, *i.e.*, for simplicity, both k_2s, *etc.* shown are considered to be equal.

then disappears as the reaction proceeds. All these observations can be reconciled by the general mechanism suggested in the Scheme and by the assumption that (a) the rate-determining steps are k_{-1} for (**5**) and k_1 or k_2 for (**1**), *i.e.*, k_{-1} (**1**) $\gg$ k_{-1} (**5**), and (b) k_2, k_{-2} (**5**) $>$ k_{-1} (**5**). The activation data, to be detailed elsewhere, support these premises: for (**5**), they are very similar to those found for the dehydrogenation (k_{-1}) of the hydrogen adduct of (**6**);[2] and the results for (**1**) are typical for an associative rate-determining step (k_1,k_2).[2] It should be finally noted that separate experiments with (**5**) + CH_3CO_2H + D_2 and (**5**) + CD_3CO_2D + H_2 in which high isotopic enrichments of the acetic acids were achieved showed through ^1H n.m.r. analyses, that only the hydroxylic hydrogen, and not the CH_3 or CD_3, is involved in the exchange.

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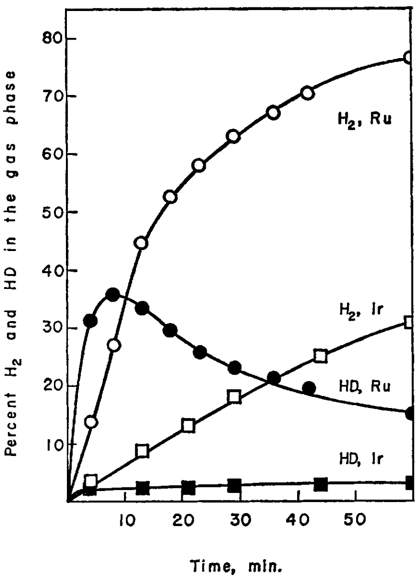

FIGURE. *The rates of exchange between* D_2 *and* CH_3COOH *catalysed by* [RuCl₂(Ph₃P)₃] (**1**) (—○—, —●—) *and* [IrH₃(Ph₃P)₃] (**5**) (—□—, —■—) *at* 25°; 2·0 × 10^{-5} *mol of complex in* 30 *ml of acetic acid;* p_{D_2} (*initial*), 700 mm; *complex:* D_2:CH_3COOH= 1:250:26,000. *Gas analysis by a chromatographic method* in situ. *The curves representing the first-order disappearance of* D_2 (99.5% *isotopic purity*) *are omitted for clarity.*

[1] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

[2] L. Vaska and M. F. Werneke, *Trans. New York Acad. Sci.*, 1971, **33**, 70.