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Preliminary communication

A KINETIC STUDY OF THE REACTION OF MONONUCLEAR Rh^{II} RHODOXIME WITH ORGANIC HALIDES

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Summary

Competition experiments have been used to evaluate rate constants for the reactions of the metal radical $Rh(dmgH)_2PPh_3$, generated by flash photolytic dissociation of alkylrhodoximes, and organic halides, which range from 1.5×10^3 M^{-1} s^{-1} ($CHCl_3$) to 4×10^6 ($CHBr_3$). The rate constants for various polyhalomethanes can be correlated with the activation energies for their reactions with atomic sodium, and are believed to occur by similar mechanisms in which halogen atom abstraction is rate-limiting.

The mononuclear Rh^{II} rhodoxime*, $Rh(dmgH)_2PPh_3$ (= M) is a 17-electron metal radical [1] which, like a number of analogous species including $Co(CN)_5{}^{3-}$ [2], $Co(dmgH)_2L$ [3], $Cr([14]aneN_4)^{2+}$ [4], and $(\eta^5\text{-}C_5H_5)W(CO)_3$ [5], reacts with organic halides by halogen atom abstraction (eq. 1):

$$M + RX \xrightarrow{k_{RX}} R\cdot + XRh(dmgH)PPh_3 \quad (= MX) \tag{1}$$

M can be produced photochemically [1] from alkylrhodoximes (eq. 2), following which it undergoes dimerization (eq. 3) at a high but measurable rate, $2k_d = 4.2 \times 10^7$ dm^3 mol^{-1} s^{-1} at low $[PPh_3]$ in ethanol at 25°C [1], but can be trapped very efficiently with $FeCl_3$ (eq. 4), and less efficiently with organic halides (eq. 1). A mixture of D and MX thus results when M is generated in the presence of RX, the proportion of each product depending upon the identity of RX and its concentration.

$$RRh(dmgH)_2PPh_3 \xrightarrow{h\nu} M + R\cdot \tag{2}$$

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*R = alkyl radical, $dmgH^-$ = monoanion of dimethylglyoxime(2,3-butane dione dioxime), rhodoxime = $Rh(dmgH)_2$.

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$$2\mathrm{M} \xrightarrow{k_d} \mathrm{D} \tag{3}$$

$$\mathrm{M} + \mathrm{FeCl_3} \rightarrow \mathrm{MCl} + \mathrm{FeCl_2} \tag{4}$$

The rate constants for a series of halides RX reacting according to eq. 1 were determined by competition experiments in which a known concentration of the $\mathrm{Rh^{II}}$ monomer, typically 3×10^{-6} mol dm^{-3}, was generated by flash photolysis, using visible light of $\lambda > 400$ nm, of ethanolic solutions of $2\text{-}\mathrm{C_3H_7Rh(dmgH)_2PPh_3}$ containing various concentrations of the desired halide. The concentration of D in the product mixture was determined immediately after the reaction (prior, however, to the onset of the slower thermal reaction between RX and D) from its intense and characteristic absorption band (λ 452 nm, $\epsilon_D = 5.0 \times 10^4$ dm^3 mol^{-1} cm^{-1}) in comparison to which the halorhodoxime product absorbs negligibly ($\epsilon_{MX} \sim 10^2$). The experiments were done in the presence of a trap for R$^{\bullet}$ such as 1-octene to prevent its recombination with M. (In contrast to the mononuclear cobaloxime system, the electronically and coordinatively saturated D does not react with R$^{\bullet}$ to form appreciable alkylrhodoxime). The data from the competition experiments were analyzed by substituting the solution of the kinetic equation $-\mathrm{d[M]}/\mathrm{d}t = 2k_d[\mathrm{M}]^2 + k_{RX}[\mathrm{RX}][\mathrm{M}]$, with $[\mathrm{RX}] \gg [\mathrm{M}]_0$ into the equation $\mathrm{d[MX]}\mathrm{d}t = k_{RX}[\mathrm{RX}][\mathrm{M}]$. Integration yields $[\mathrm{MX}]_\infty = A^{-1} \ln([\mathrm{M}]_0 A + 1)$ where $A = 2k_d/k_{RX}[\mathrm{RX}]$. From the stoichiometric relationship $2[\mathrm{D}]_\infty + [\mathrm{MX}]_\infty = [\mathrm{M}]_0$ it follows that the product ratio is given by eq. 5.

$$R_\infty = \frac{[\mathrm{D}]_\infty}{[\mathrm{MX}]_\infty} = \frac{[\mathrm{M}]_0 - A^{-1} \ln([\mathrm{M}]_0 A + 1)}{2A^{-1} \ln([\mathrm{M}]_0 A + 1)} \tag{5}$$

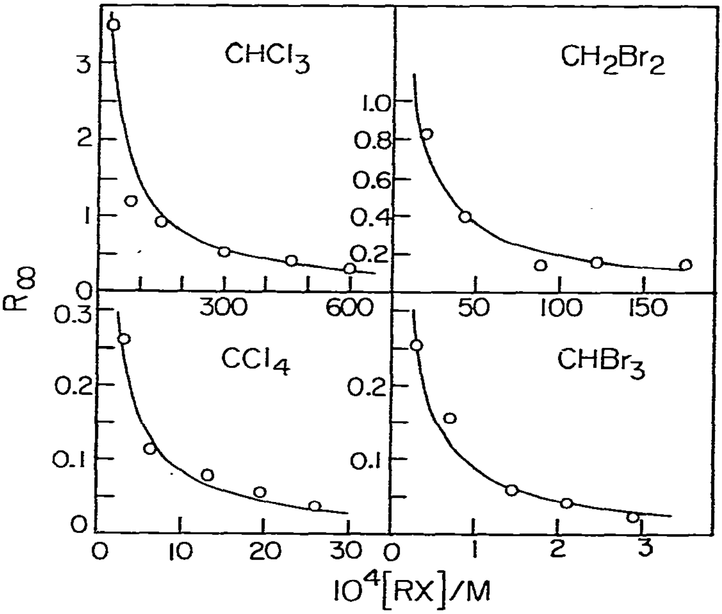

Fig. 1. The product ratios for four reactions are shown as a function of concentration. The smooth curves are the theoretical ones corresponding to the values of k_{RX} given in Table 1.

TABLE 1

RATE CONSTANTS[a] FOR REACTION 1

RX	Conc. range	k_{RX} (dm^3 mol^{-1} s^{-1})
$CHBr_3$	2.9 to 29 × 10^{-5}	4.0 × 10^6
CCl_4	2.6 to 26 × 10^{-4}	2.5 × 10^5
$PhCH_2Br$	2.1 to 24 × 10^{-4}	2.5 × 10^5
CH_2Br_2	1.8 to 18 × 10^{-3}	1.3 × 10^4
$i\text{-}C_3H_7Br$	2.7 to 27 × 10^{-3}	5.0 × 10^3
$CHCl_3$	3 to 60 × 10^{-3}	1.5 × 10^3

[a] In ethanol at ~25°C; uncertainty in k_{RX} is ±20%.

The range of suitable RX concentrations needed to produce a balanced competition is different for each case since k_{RX} varies widely; indeed, this places a restriction on the particular halides which could be studied. Figure 1 depicts for four of the compounds the experimental values of R_∞ as a function of [RX]. The resulting values of k_{RX} are given in Table 1. The mechanism of the halogen abstraction reactions of eq. 1 is believed to be the same as that of the corresponding gas-phase reactions of sodium atoms (eq. 6):

$$\mathrm{Na} + \mathrm{RX} \rightarrow \mathrm{NaX} + \mathrm{R}^{\bullet} \qquad (6)$$

Fukui [6,7] has treated the transition states for radical displacement processes ($RX + R'^{\bullet} \rightarrow [R\cdots X \cdots R']^{\ddagger}$) in terms of delocalizability parameter D_r and thus realized a successful correlation of the rate constants and activation energies for sodium atom reactions, eq. 6, and analogous reactions of alkyl radicals. One might expect k_{RX} for the polyhalomethanes and D_r to be similarly correlated; but this cannot be tested because the practical limitations of the present experiments limited the determinations to compounds having k_{RX} between ca. 10^3 and 10^7 dm^3 mol^{-1} s^{-1}. On the other hand, a direct comparison between reactions 1 and 6 is an equivalent formulation since E_{a6} is known independently to correlate with D_r. Figure 2 depicts a plot of ln k_{RX} for the four polyhalomethanes versus the activation energies for their reactions with sodium. The linearity of this graph serves to affirm the correctness of this analysis.

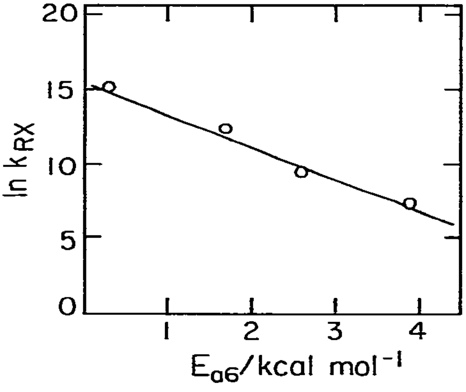

Fig. 2. Plot of ln k_{RX} for polyhalomethanes versus the activation energies for eq. 6.

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