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KINETICS AND MECHANISM OF DECOMPOSITION OF PHENYLPROPYLBIS(DIMETHYLGLYOXIMATO)PYRIDINECOBALT(III) IN AQUEOUS SULPHURIC ACID

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Summary

The kinetics of formation of (*E*)-1-phenylpropene and radical dimers from 1-phenylpropylcobaloxime, 2-[$^2H_1$]-1-phenylpropylcobaloxime and 2-[$^2H_2$]-1-phenylpropylcobaloxime have been determined in aqueous sulphuric acid, mainly under conditions where the conjugate acid is the predominant reactive species. The proportion of olefin in the product is less from the deuteriated than from the undeuteriated substrates and the extent of deuteriation of the olefin formed from the monodeuteriated substrate is indicative of a stereospecific elimination of the metal hydride. The results are consistent with a mechanism which involves the reversible formation of a radical pair which can either lose cobaloxime(II), leading to the dimer of the organic radical, or can undergo a hydride abstraction within the solvent cage to give olefin. The mechanism is supported by the influence of substituents on the rate of reaction of substituted phenylethylcobaloximes under the same conditions.

Previous kinetic studies of the decomposition of phenylethylcobaloximes have clearly indicated that homolysis of the carbon–cobalt bond plays an important but not unambiguously dominant role. Thus Halpern has noted that the enthalpy of activation for the decomposition, in toluene under a nitrogen purge, of phenylethylbis(dimethylglyoximato)pyridinecobalt(III) (**1**) to styrene, hydrogen and bis(dimethylglyoximato)cobalt (II) (**2**; eq. 1) is only slighly greater than the dissociation energy calculated for that carbon–cobalt bond (i.e. $\Delta H^{\ddagger}$ 21.2 ± 5 kcal/mol; D(Co–C) 19.9 kcal/mol) [1] and has concluded that, as the difference is compatible with the enthalpy of activation for the capture of the phenylethyl radical by the cobaloxime(II)

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radical **2**, homolysis of the carbon–cobalt bond is likely to be the rate-determining step in the olefin formation. Gjerde and Espenson have observed products clearly derived from phenylethyl radicals in the decomposition of complex **1** in aqueous methanolic perchloric acid, under conditions where any cobaloxime(II) formed is rapidly destroyed by the excess of acid, but they were unable to show that the styrene was not formed by an independent concurrent non-radical path [2]. Similarly, though phenylethyl and 2-[$^2H_3$]-phenylethyl radicals have been trapped by nitrones and nitroso compounds during the decomposition of phenylethylcobaloximes, that provides no evidence directly to indicate that they should lead to olefin formation [3]. On the other hand, our studies of the stereochemistry of addition of hydridocobaloxime to indene and to (*E*)-1-phenylpropene and of the decomposition of isotopically-substituted 1-phenylpropylbis(dimethylglyoximato)pyridinecobalt-(III) (**4**) in several solvents have indicated that both the addition and its reverse are free radical processes [4].

In this paper are described studies of the decomposition of the conjugate acid of phenylpropylcobaloxime and some of its isotopically-substituted analogues in order to determine kinetic and product isotope effects and to shed more light on the stereochemistry of the addition reaction and its reverse. Some related reactions of benzyl- and substituted phenylethyl-cobaloximes are also described.

Results

Decomposition of benzylbis(dimethylglyoximato)pyridinecobalt(III) in aqueous sulphuric acid

The kineticss of decomposition of benzylbis(dimethylglyoximato)pyridine-cobalt(III) (**3**, ca. 10^{-5} *M*) under aerobic conditions in aqueous sulphuric acid at 25°C were determined as a function of the acid concentration (0.61–9 *M*). First order kinetics were observed; the rate constants are shown in Table 1. The main organic products of decomposition of complex **3** (10^{-3} *M*) in aqueous sulphuric acid at $H_0 = -3.9$ were benzaldehyde, benzyl alcohol and traces of the *O*-benzyl derivative of diacetylmonoxime. As the concentration of benzylcobaloxime was increased above that of the available oxygen, dibenzyl was formed in substantial quantities, and in concentrated solution was the major product.

Decomposition of phenylpropylcobaloxime in aqueous sulphuric acid.

The kinetics of anaerobic decomposition of phenylpropylcobaloxime (**4**-H_2) in aqueous sulphuric acid (0.61–7.3 *M*) and of aerobic decomposition in 0.61 *M* sulphuric acid were studied at 5°C. The reactions were first order in substrate; the rate coefficients are shown in Table 2. The main products of decomposition of complex **4**-H_2 in 0.61 *M* acid (i.e. $H_0 = 0$) were (*E*)-1-phenylpropene (**5**) and

TABLE 1

KINETICS OF AEROBIC DECOMPOSITION OF BENZYLCOBALOXIME IN AQUEOUS SULPHURIC ACID AT 25°C.

% H_2SO_4 (w/w)	5	17	31.5	44.1	55.1	64.8	81.1	88
$-H_0$	0	0.9	1.95	2.9	3.9	5.1	7.6	8.8
$10^4\ k/s^{-1}$	0.4	0.58	1.7	3.7	5.5	6.7	7.1	7.5

TABLE 2

KINETICS AND PRODUCTS OF ANAEROBIC DECOMPOSITION OF PHENYLALKYLCOBALOXIMES PhCHRCo(dmgH)$_2$py IN AQUEOUS SULPHURIC ACID AT 5°C.

$-H_0$	R = CH_3		R = CH_2CH_3		R = $CHDCH_3$		R = CD_2CH_3	
	$10^3\ k/s^{-1}$	olefin/dimer	$10^3\ k/s^{-1}$	olefin/dimer	$10^3\ k/s^{-1}$	olefin/dimer	$10^3\ k/s^{-1}$	olefin/dimer
0	0.138	27/73 [a]	0.43(0.52) [b]	77/23	0.33	69/31	0.29	62/38
1			0.69					
2			1.22					
3			2.39					
4			2.97					
5			3.37					

[a] Determined in 1 *M* $HClO_4$ in 40% aqueous methanol [2]. [b] In the presence of oxygen.

dimers of the phenylpropyl radical (mainly, but not exclusively, the dimers **6a** and **6b** in equimolar amounts). The proportions of olefin to total dimer are shown in Table 2. The kinetics and products of the anaerobic decomposition of 2-[$^2H_2$]-phenylpropylcobaloxime (**4**-D_2) and of an 85/15 mixture of diastereoisomers of 2-[$^2H_1$]-phenylpropylcobaloxime (**4**-HD-c and **4**-HD-t) were also determined in 0.61 *M* sulphuric acid. The results are shown in Table 2. The product of aerobic decomposition of phenylpropylcobaloxime (**4**-H_2) in 0.61 *M* sulphuric acid was substantially a near-equimolar mixture of 1-phenylpropanol and 1-phenylpropanone; the same products as were formed in the markedly slower decomposition of phenylpropylperoxycobaloxime (**7**) in 0.61 *M* aqueous sulphuric acid. The complex **7** could be recovered substantially unchanged after several minutes in 0.61 *M* sulphuric acid at ambient temperature.

Decomposition of substituted phenylethylcobaloximes in aqueous sulphuric acid

The kinetics of anaerobic decomposition of 4-fluoro-, 3-chloro-, 4-chloro-, 4-bromo-, 4-methyl-, and 4-methoxy-phenylethylcobaloximes in 0.61 *M* aqueous sulphuric acid were also determined at 5 and/or 15°C. The products of these reactions were not determined. The first order rate constants obtained are shown in Table 3.

TABLE 3

KINETICS OF DECOMPOSITION OF 3- AND 4-SUBSTITUTED PHENYLETHYLCOBALOXIMES ($XC_6H_4CHMe\cdot Co(dmgH)_2py$) IN 0.61 *M* AQUEOUS SULPHURIC ACID

Temperature (°C)	X	$10^4\ k/s^{-1}$	log k_{rel}	σ^+	$\sigma_\alpha^\cdot$
15	4-F	9.4	−0.05	−0.07	−0.011
15	3-Cl	10	−0.02	0.40	0.001
15	H	10.5	0	0	0
15	4-Br	10.8	0.02	0.15	(0.004) [a]
15	4-Me	12.9	0.09	−0.31	0.015
15	4-Cl	15.2	0.16	0.11	0.017
5	4-OMe	2.12	0.43 [b]	−0.78	0.034

[a] Derived using eq. 6. [b] Determined using a value of $1.38\times10^{-4}\ s^{-1}$ for the parent compound at 5°C.

Discussion

Character of the complexes in aqueous sulphuric acid

Several workers have shown, mainly from a consideration of the influence of pH on the rates of oxidative and electrophilic reactions of alkylcobaloximes [5,6,7,8], that one of the equatorial dioximato ligands is protonated in the region of pH = 1 (eq. 2). A pK_a of 0.91 has been estimated for phenylethylbis(dimethylglyoximato)-aquocobalt(III) (**9**; L = aq, R = $PhCHCH_3$) in 40% aqueous methanolic perchloric acid. It has also been shown that the pyridine ligand is rapidly removed and replaced by water in aqueous acidic solutions [9], and that any cobaloxime(II) or hydridocabaloxime formed in strongly acidic solution is rapidly destroyed [2,10], but the extent to which counter-ions, including bisulphate ion, may coordinate to the cationic complexes **9** and **10** has not been established. Similarly, no detailed investigation has been attempted of the second protonation (**9** ⇌ **10**) of the di-oximato ligands in more acidic solution.

$$\underset{(\mathbf{1})}{PhCH(CH_3)Co(dmgH)_2py} \xrightarrow{\text{toluene}} PhCH{=}CH_2 + \tfrac{1}{2}H_2 + \underset{(\mathbf{2})}{Co^{II}(dmgH)_2py} \qquad (1)$$

$$\underset{(\mathbf{3})}{PhCH_2Co(dmgH)_2py} \xrightarrow[H^+]{O_2} PhCHO + PhCH_2OH + (PhCH_2CH_2Ph) \qquad (2)$$

$$PhCH(CH_3)Co(dmgH)_2py \xrightarrow[H^+]{N_2} PhCH{=}CH_2 + \underset{(\mathbf{3a}\text{ and }\mathbf{3b})}{PhCH(CH_3)CH(CH_3)Ph} \qquad (3)$$

$$\underset{(\mathbf{8})}{RCo(dmgH)_2L} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \underset{(\mathbf{9})}{[RCo(dmgH_2)(dmgH')L]^+} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \underset{(\mathbf{10})}{[RCo(dmgH_2)_2L]^{2+}} \qquad (4)$$

The variation of the first order rate constants both for the aerobic decomposition of benzylcobaloxime and the anaerobic decomposition of phenylpropylcobaloxime (Tables 1 and 2, and Fig. 1), shows clearly that there is a second protonation in the region of $H_0 = -2$ to -3, implying that the complex **10** (R = PhCHEt or $PhCH_2$; L = aq) has a pK_a of ca. -2.5. It is unlikely that bisulphate ion complexes exist substantially in this region of acidity [11]. We therefore chose to work at one main acidity, namely at $H_0 = 0$, where the predominant species is the monoconjugate acid of the organocobaloxime (i.e. **9**), the proportion of the less reactive neutral complex being small and that of the more reactive diconjugate acid (**10**) negligible. The rate constants and products obtained for this acidity should thus reflect almost exclusively the reactions of the conjugate acid **9**.

The products of decomposition of benzylcobaloxime in strongly acidic solution ($H_0 = -3.9$) depended on the concentration and conditions. Where a deficiency of oxygen was present, the yield of dibenzyl was substantial, but in the presence of an excess of oxygen, the products of oxidation of the benzyl radical and of hydrolysis of benzylperoxycobaloxime were formed. Clearly, the main pathway for decomposition of benzylcobaloxime in acidic solution, under conditions where any cobaloxime(II) is rapidly destroyed, is by homolysis of the carbon–cobalt bond. The products of the corresponding reaction of phenylethyl and phenylpropylcobaloximes in strongly acidic solution proved numerous and difficult to characterise;

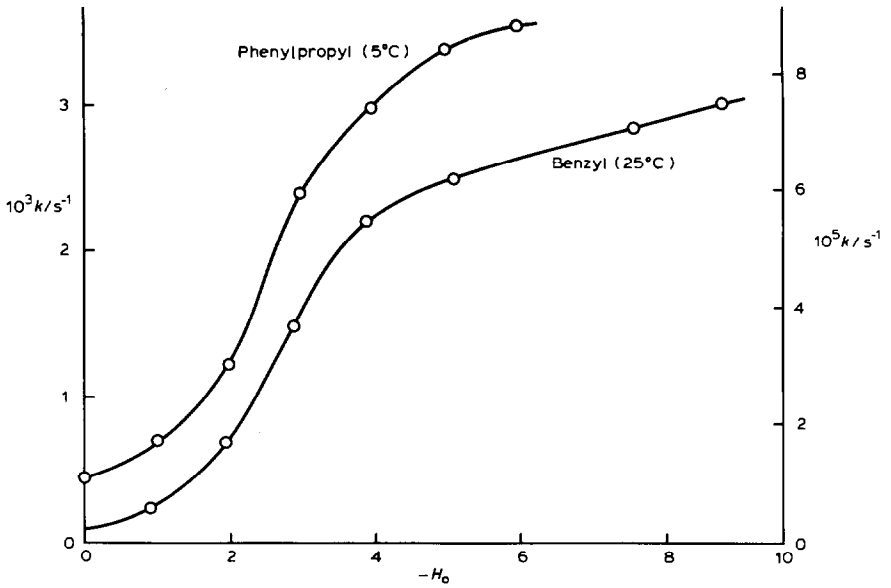
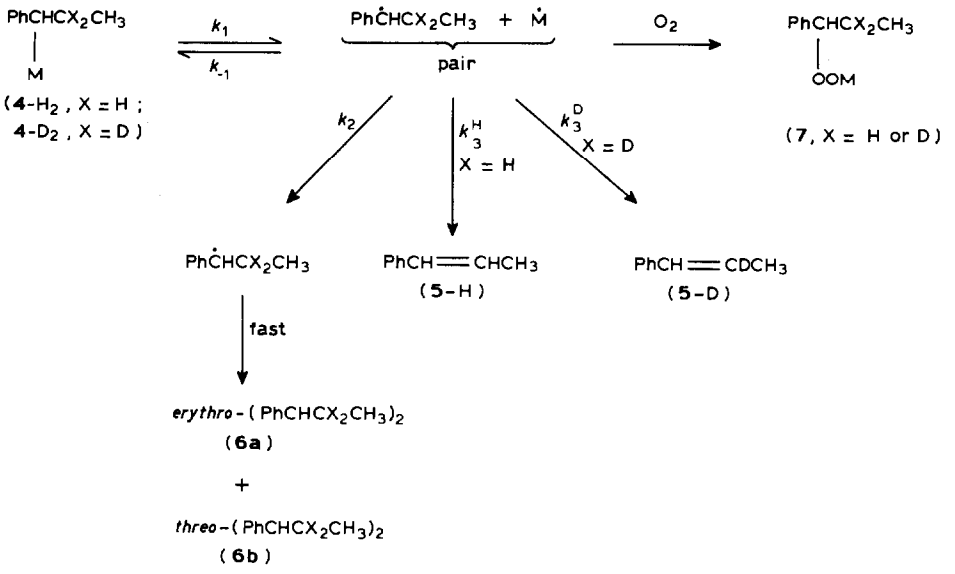


Fig. 1. First order rate coefficients for the aerobic decomposition of benzylbis(dimethylglyoximato)-pyridinecobalt(III) at 25°C (right hand scale) and for the anaerobic decomposition of 1-phenylpropylbis(dimethylglyoximato)pyridinecobalt(III) and 5°C (left hand scale) in aqueous sulphuric acid.

probably because of polymerisation of the olefin formed. However, when phenol was present (either added or formed during the acid catalysed decomposition of phenylalkylperoxycobaloximes present as impurity in some samples **1** and **4**), the main products were the 1-phenylalkanol, 1-phenylalkanone and mono-, di-, and tri-substituted (alkylphenyl)phenols. Clearly, the styryl and phenylpropyl cations are formed under these circumstances, but it is not certain whether these arise through prior formation of the olefin or of the alcohol, or are direct products of the heterolytic decomposition of the diprotonated complexes (**10**; R = $PhCHCH_3$ or PhCHEt).

Whereas the anaerobic decomposition of 1-phenylethylcobaloxime in 1 *M* aqueous methanolic perchloric acid at 25°C gave significantly higher yields of the dimers (mainly **3a** and **3b** together with other isomers; total yield 73%) than of the olefin, styrene (27%) [2], the corresponding decomposition of 1-phenylpropylcobaloxime (**4**-H_2) in aqueous sulphuric acid gave a much higher yield of the olefin, (*E*)-1-phenylpropene (**5**-H; 77%), than of the dimers (mainly **6a** and **6b**; 23%). The main organic product in the latter case was that derived by acid catalysed decomposition of the equatorial dioximato ligands, namely diacetyl monoxime. Neither 1-phenylpropane nor (*Z*)-1-phenylpropene could be detected in the reaction products by 250 MHz NMR spectroscopy or by GLC/mass spectrometry thus indicating that conformational preference rather than isotopic selection determines the olefin formed, and that under these conditions the 1-phenylpropyl radical dimerises much more readily than it disproportionates. The products formed in the decomposition of phenylpropylcobaloxime in 0.61 *M* acid under aerobic conditions are indicative



SCHEME 1

of the formation of phenylpropyl radicals and the phenylpropylperoxycobaloxime as intermediates. Since, under partially anaerobic conditions, little change in either the rate of decomposition or the relative yields of olefin and dimers could be detected, capture of the free radical by oxygen, and/or phenylpropylperoxycobaloxime formation must occur prior to any olefin/dimer forming steps.

Under comparable conditions in 0.61 *M* acid, the relative yield of the deuterated olefin **5**-D from the dideuterated phenylpropylcobaloxime **4**-D_2 was lower than that of the olefin **5**-H from **4**-H_2; the yield of **6**-D_4 being accordingly higher than that of **6**-H_4, respectively. This clearly shows that there is an isotope effect in the formation of the olefin. No isotope effect, other than a negligible secondary isotope effect, would be expected for homolysis of the carbon–cobalt bond, for the separation of a radical pair, for the dimerisation of the organic radical, or for the recombination of the organic radical and cobaloxime(II) within or without the solvent cage. The variation in the olefin/dimer product ratio thus suggests that k_3^H/k_2 (see Scheme 1) has the value 1.6 and that k_3^D/k_2 has the value 0.79 (since each molecule of dimer is derived from two organic radicals), and hence that there is a true isotope effect $k_3^H/k_3^D \sim 2$ in the olefin forming step from the radical pair.

The overall kinetic isotope effect $(k_H/k_D)_{obs}$ determined using the steady state approximation as applied to Scheme 1 is given by eq. 5. In Table 4 are shown those values of this overall isotope effect calculated using a range of values for the unknown quantity k_{-1}/k_2 and for the experimentally determined quantities k_3^H/k_2 and k_2^D/k_2. The results show that the kinetically measured value of $(k_H/k_D)_{obs}$ of 1.4 is compatible with the mechanism shown in Scheme 1, but is also relatively independent of the value of k_{-1}/k_2. However, it is unlikely that k_1/k_2 is very large, because the rate of decomposition of phenylpropylcobaloxime in the presence

TABLE 4

CALCULATED KINETIC ISOTOPE EFFECT FOR A SELECTION OF VALUES OF k_{-1}/k_2, k_3^H/k_2, and k_3^D/k_2

k_{-1}/k_2	k_3^H/k_2	k_3^D/k_2			
		0.5	0.75	0.79 [a]	1.0
2	2	1.40	1.29		1.20
8	2	1.73	1.52		1.36
20	2	1.87	1.62		1.43
100	2	1.97	1.69		1.49
2	1.6 [a]			1.20	
8	1.6 [a]			1.34	
20	1.6 [a]			1.40 [b]	
100	1.6 [a]			1.44	
2	1.3	1.24	1.14		1.07
8	1.3	1.41	1.24		1.11
20	1.3	1.49	1.27		1.14
100	1.3	1.52	1.31		1.15

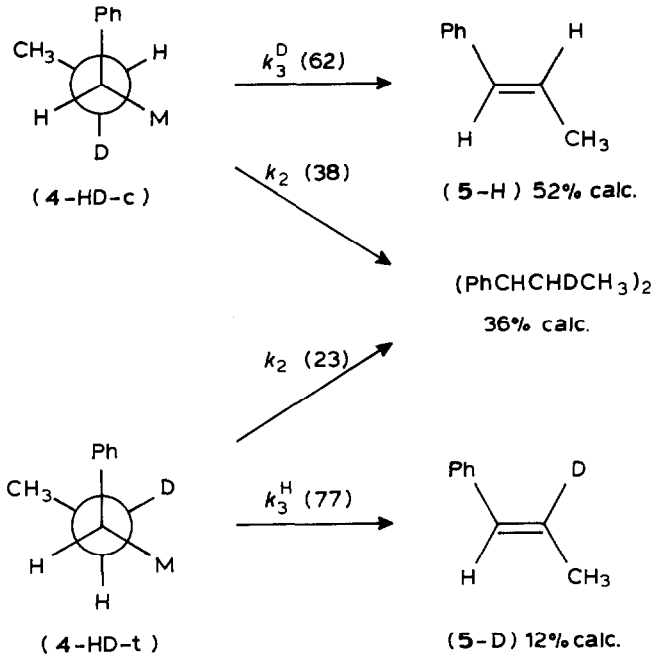
[a] Values determined from product ratios. [b] Coincidental with overall kinetic isotope effect experimentally determined.

of air is only slightly (× 1.2) faster than under anaerobic conditions, and oxygen is undoubtedly an excellent free radical trap.

$$(k_H/k_D)_{obs} = \frac{(k_2 + k_3^H)}{(k_2 + k_3^D)} \cdot \frac{(k_{-1} + k_2 + k_3^D)}{(k_{-1} + k_2 + k_3^H)} \quad (5)$$

One of the key experiments, however, is the determination of the character of the olefin formed from the decomposition of the monodeuterated mixture of diastereoisomers **4**-HD. Whereas the complex **4**-H_2 must give dimers and the olefin **5**-H and complex **4**-D_2 must give dimers and the olefin **5**-D, the 85/15 mixture of **4**-HD-c and **4**-HD-t should, if the reaction is stereospecific, give a mixture containing 80% **5**-H and 20% **5**-D, i.e. that determined by the relative rates of formation of olefin and dimer from each of the two diastereoisomers as shown in Scheme 2. Moreover, if the reaction is stereospecific the yields of olefin and dimer from **4**-HD-c should be determined by the same relative rate constants (k_2 and k_3^D) as observed for **4**-D_2, and the yields from **4**-HD-t should be determined by the same relative rate constants (k_2 and k_3^H) as observed for **4**-H_2. If the reaction is not stereospecific, the olefin formed from the diastereoisomeric mixture should contain appreciably more of the mono-deuterated species **5**-D. In the actual decomposition of the diastereoisomeric mixture, the yield of olefin was 69% compared with a calculated yield of 64% and it contained slightly less than the 20% **5**-D anticipated. In contrast, the olefin formed from the decomposition of the diastereoisomeric mixture of **4**-HD-c and **4**-HD-t in $CDCl_3$ under partially aerobic conditions, which takes place by a different mechanism, contained 50% **5**-H, indicating a random removal of hydrogen and deuterium. Clearly, the anaerobic decomposition of phenylpropylcobaloxime in 0.61 *M* sulphuric acid is stereospecific or, at least, substantially stereoselective.

It is thus clear that the decomposition of the diastereoisomeric mixture of **4**-HD-c and **4**-HD-t should not show clean first order kinetics, because the overall process is a mixture of two independent reactions of different rate constants.



SCHEME 2

However, the presence of a mere 15% of the faster reacting isomer and 85% of that isomer reacting only some 1.5 times more slowly ensured that the deviation from first order kinetics was insufficient to be detected under our experimental conditions.

One can thus conclude, from the overall rates of reaction and the relative proportions of olefin and dimer formed in the reactions of phenylpropyl and phenylethylcobaloximes, that the overall rate constant for the formation of radical dimers is almost identical for each of the two complexes (k = ca. 1×10^{-4} s^{-1}), in accord with the anticipated similarity of bond strengths and rates of separation of radical pairs, whereas the rate of formation of phenylpropene from the phenylpropylcobaloxime (k = ca. 3×10^{-4} s^{-1}) is an order of magnitude greater than that for the formation of styrene from phenylethylcobaloxime (k = ca. 3×10^{-5}, s^{-1}), in accord with the expected greater facility for the formation of a 1,2-disubstituted olefin compared with that for the formation of the corresponding mono-substituted olefin.

The influence of *meta*- and *para*-substituents on the rates of reaction of the phenylethylcobaloximes in 0.61 *M* sulphuric acid proved to be rather slight, and any detailed discussion of substituent effects is not justified. However, of the available Hammett and related linear free energy relationships, the best fit with the experimental data shown in Table 3 was obtained using eq. 6 with the substituent constants $\sigma_\alpha^\cdot$ derived from the influence of substituents on the hyperfine coupling constants of benzyl radicals [12], and modified by the inclusion of a term incorporating the Brown and Okamoto substituent constant σ^+ [13].

$$\log(k/k_H) = \rho^+\sigma^+ + \rho^\cdot\sigma_\alpha^\cdot \qquad (6)$$

The ratio $\rho^{\cdot}/\rho^{+}$ is thus a function of the radical character of the transition state. The results in Table 3 give a moderate correlation with $\sigma_{\alpha}^{\cdot}$ alone without recourse to σ^{+} ($\rho^{\cdot} = 12.6$; correlation coefficient 0.907), but a better correlation with $\rho^{\cdot} = 8.86$ and $\rho^{+} = -0.095$ (correlation coefficient 0.967), in accord with, but by no means verifying, the mechanism shown in Scheme 1. Less satisfactory correlations were obtained with those substituent constants derived from (i) abstraction of a hydrogen atom from substituted cumenes by polystyryl radicals [14] (ii) the addition of trichloromethyl radicals to substituted styrenes [15], and (iii) the abstraction of hydrogen atoms from substituted toluenes by bromine atoms [16].

Experimental

Preparation of organic precursors. Propiophenone was deuterated by the method of Streitweiser [17], until the proton NMR signal at δ 3 ppm could no longer be detected. 2-[$^{2}H_{2}$]-Propiophenone was reduced by lithium aluminium hydride in ether to 2-[$^{2}H_{2}$]-1-phenylpropanol (90%) and then to 2-[$^{2}H_{2}$]-1-chloro-1-phenylpropane (42%) using thionyl chloride and pyridine at 0°C.

Preparation of organocobaloximes. 1-Phenylethyl- [4], 1-phenylpropyl- [4], 1-(4-fluorophenyl)ethyl- [18], 1-(4-methylphenyl)ethyl- [18], 1-(4-chlorophenyl)ethyl- [18], 1-(3-chlorophenyl)ethyl- [18], 1-(4-bromophenyl)ethyl- [18], and 1-(4-methoxyphenyl)ethyl-bis(dimethylglyoximato)pyridinecobalt(III) [18] were prepared in from 35–86% yield by the addition of sodium borohydride to a suspension of the corresponding substituted styrene and chlorobis(dimethylglyoximato)pyridinecobalt(III) in 1/1 aqueous methanol a 0°C. The precipitate of the organocobaloxime was filtered off, washed copiously with cold water, pentane, and more cold water until the latter was colourless, and dried in vacuo. All the above cobaloximes had previously been reported. 2-[$^{2}H_{2}$]-1-phenylpropylbis(dimethylglyoximato)pyridinecobalt(III) was prepared as above, but using *O*-[$^{2}H_{2}$]-chlorobis(dimethylglyoximato)pyridinecobalt(III) and a 1/1 mixture of MeOD and $D_{2}O$ (yield 27%). The diastereoisomeric mixture of 2-[$^{2}H_{1}$]-1-phenylpropylcobaloximes was prepared as described earlier [4]. Benzylbis(dimethylglyoximato)pyridinecobalt(III) was prepared by standard methods.

Determination of reaction products. Benzylcobaloxime (100 mg) was dissolved in air-saturated 50% aqueous sulphuric acid (100 ml) and allowed to stand in the dark for 4 h at ambient temperature. The solution was diluted with an equal volume of water and extracted with methylene chloride and ether. The organic phase was washed with water containing 1% pyridine and with water, dried ($Na_{2}SO_{4}$) and the solvent was removed in vacuo. The ^{1}H NMR spectrum of the product was measured at this stage and after each step in pentane extraction and chromatography on silica gel (Malincrodt CC7). The products were benzaldehyde (29%) benzyl alcohol (13%), unchanged benzylcobaloxime (55%) and minor products including *O*-benzyldiacetyl monoxime. Using benzylcobaloxime (10^{-2} *M*) the main product was dibenzyl.

Phenylpropylcobaloxime (100 mg) and aqueous sulphuric acid (0.61 *M*; 100 ml) were placed in separate parts of a double reservoir flask. The flask was repeatedly degassed at −120°C and refilled with oxygen-free nitrogen or argon. The cobaloxime was added to the acid and the solution was left overnight and worked up as above. The products were identified by ^{1}H NMR spectroscopy (Bruker 250 MHz) and by GLC Mass spectrometry (Ribermag R-10-10), the principle products, in

order of elution being (given in the sequence: relative area of GLC peak, principle *m/e* (intensity)):

From phenylpropylcobaloxime: (*E*)-1-phenylpropene, 528; *m/e* 118(72), 117(100), 115(39), 91(24). Dimer 1, 70; *m/e* 119(67), 118(58), 91(100). Dimer 2, 83; *m/e* 119(68), 118(58), 91(100). Other dimers, 16; *m/e* inaccurate.

From 2-[$^2H_2$]-1-phenylpropylcobaloxime: (*E*)-1-phenylpropene, 265; *m/e* 119(77), 118(100), 117(15), 116(32), 115(10). Dimer 1, 83; *m/e* 122(11), 121(100), 120(9), 119(85), 92(100). Dimer 2, 83; *m/e* 122(11), 121(85), 120(12), 119(81), 92(100). Other dimers, 22.

From 2-[$^2H_1$]-1-phenylpropylcobaloxime: (*E*)-1-phenylpropene, 403; *m/e* 119(17), 118(84), 117(100), 116(13), 115(42). Dimer 1, 68; *m/e* 120(33), 119(56), 118(48), 91(100), 92(28). Dimer 2, 80; *m/e* 120(38), 119(66), 118(53), 91(100), 92(28). Other dimers, 26.

Kinetic measurements. The aqueous sulphuric acid and the solid cobaloxime were repeatedly degassed (5×10^{-3} mmHg) at liquid nitrogen temperature, allowed to attain the appropriate reaction temperature, mixed and shaken until all the solid had dissolved. The rate constants were determined by standard first order methods from observations of the decrease in absorption at 368 nm. Values of H_0 were taken from ref. 20.

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