Reactivity of Bridgehead Halides with Pentacyanocobaltate(II)

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The kinetics of the reaction of pentacyanocobaltate(II) with 1-adamantyl iodide and 2,4-dimethyl-1-bicyclo[2.2.2]-octyl iodide are studied and found to be second order in pentacyanocobaltate(II) and first order in the iodide. When studied in the presence of acrylonitrile as a radical scavenger the kinetics then show the usual first-order dependence on each of pentacyanocobaltate(II) and organic iodide. A comparative study is also performed on the rates of reaction of other bridgehead halides *e.g.* 7,7-dimethyl-1-bicyclo[2.2.1]heptyl iodide and triptycyl iodides. The reactivities of the iodides decrease in the order of the relative stability of the bridgehead radicals (second-order rate constants at 25 °C in $dm^3 mol^{-1} s^{-1}$ given in parentheses): 1-adamantyl (2.47×10^{-2}) > 2,4-dimethyl-1-bicyclo[2.2.2]octyl (7.5×10^{-3}) > 7,7-dimethyl-1-bicyclo[2.2.1]heptyl ($< 10^{-6}$) > triptycyl ($< 10^{-6}$).

BRIDGEHEAD reactivity has always attracted considerable theoretical as well as experimental interest; bridgehead carbonium ions, in particular, have been extensively studied [1] while many comparative studies of bridgehead radicals have also been reported.[2] High reactivity has generally been observed for these species if they can be generated successfully. On the other hand, bridgehead anionic species are, as may be expected, relatively stable and some of these have served as intermediates in the syntheses of highly strained bridgehead olefins or ' Bredt ' compounds.[3,4] Organometallic derivatives bonded to bridgehead carbons may also be expected to show moderate stability since their decomposition would lead to unstable Bredt compounds or else to high-energy radical intermediates. Indeed, first examples of bridgehead organocobalt and organochromium complexes have been reported recently.[5-7]

The syntheses of 1-adamantyl and 1-bicyclo[2.2.2]-octyl pentacyanocobaltates reported earlier [5,6] involved the reaction of pentacyanocobaltate(II) with the respective organic iodides. These bridgehead organic halides react at various rates. The earlier work of Halpern [8] has established that the reaction of pentacyanocobaltate(II) with several organic halides is radical in nature, where halogen-atom abstraction by $Co(CN)_5^{3-}$ is the rate-determining step, so that in the presence of an excess of organic halide, RX, the kinetics are always first order in pentacyanocobaltate(II). The present study on the comparative reactivity of bridgehead halides demonstrates that for these less reactive compounds, the kinetics show considerable deviation from the usual first-order dependence on pentacyanocobaltate(II).

RESULTS AND DISCUSSION

The bridgehead halides (1)—(5) were synthesized and treated with pentacyanocobaltate(II) in 80% methanolic solution. The products from 1-adamantyl iodide (1) and 2,4-dimethyl-1-bicyclo[2.2.2]octyl iodide (2) showed that the stoicheiometry is in accord with that established by Halpern,[8] depicted in equation (1). However, in

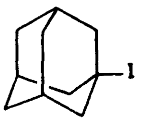
$$2Co(CN)_5^{3-} + RX \longrightarrow RCo(CN)_5^{3-} + Co(CN)_5X^{3-} \quad (1)$$

contrast to Halpern's findings, the reaction of (1) and (2) with $Co(CN)_5^{3-}$ exhibited second-order dependence on $[Co(CN)_5^{3-}]$, the kinetics when the organic iodide is in a ten-fold excess over $Co(CN)_5^{3-}$ being adequately described by equation (2) for up to two half-lives of the

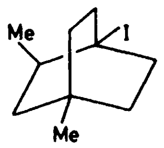
$$\text{Rate} = -d[Co(CN)_5^{3-}]/dt = k_{obs.}[Co(CN)_5^{3-}]^2 \quad (2)$$

reaction, where $k_{obs.} = 2k[RX]/[Co(CN)_5^{3-}]_0$ and $[Co(CN)_5^{3-}]_0$ is the initial concentration of pentacyanocobaltate.

Typical plots of $1/[Co(CN)_5^{3-}]$ and $\log[Co(CN)_5^{3-}]$ against time are illustrated in Figures 1—3. Under the reaction conditions it was also checked that the decomposition of $Co(CN)_5^{3-}$ in water was not significant enough to affect the above kinetic data; neither was catalysis by light of the spectrophotometer detected. Values of $k_{obs.}$ determined from the slopes of plots of $1/[Co(CN)_5^{3-}]$ against time, together with the corresponding values of computed k, are listed in Table 1.



(1)



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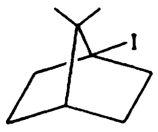

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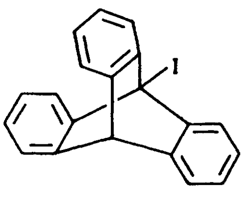

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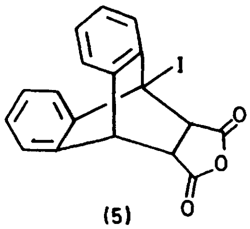

(5)

In the presence of acrylonitrile, the kinetics observed were second order, being first order in each of $Co(CN)_5^{3-}$ and RX, as reported for a large number of simple halides.[8] Typical linear plots of $\log[Co(CN)_5^{3-}]$ against time are shown in Figures 1 and 2 and the values of $k'_{obs.}$ obtained from their slopes are listed in Table 2. These are in agreement with a rate law defined by equation (3).

The results on the effect of acrylonitrile indicate that a

TABLE 1

Kinetic data for the reaction of 1-amantyl iodide and 2,4-dimethyl-1-bicyclo[2.2.2]octyl iodide with $Co(CN)_5^{3-}$ in the absence of acrylonitrile at 25 °C in 80% MeOH

Organic halide RX	Initial reactant concentrations/10^{-3} mol dm^{-3} $[Co(CN)_5^{3-}]$	[RX]	$k_{obs.}$/dm^3 mol^{-1} s^{-1} [a]	10^3 k/dm^3 mol^{-1} s^{-1} [b]	10^3 k/s^{-1} [c]	$10^3 k'_1$/dm^3 mol^{-1} s^{-1} [d]
(1) 1-Adamantyl iodide	1.8	13.59	0.561	37.1	0.76	28
	1.8	21.45	0.874	36.7	1.2	28
	3.4	28.56	0.576	34.3	1.5	26
	3.1	37.50	0.725	30.1	1.9	25
	1.5	15.57	0.705	33.9	0.76	24
	2.0	25.25	0.869	34.4	1.3	25
				average 34.4 ± 2.3		k_1 (average) 26 ± 2
(2) 1-Bicyclo-octyl iodide	1.6	44.98	0.520	9.3	0.61	6.8
	1.5	16.99	0.211	9.3	0.22	6.6
	1.4	17.94	0.210	8.1	0.23	6.4
	2.6	28.25	0.188	8.6	0.35	6.1
	2.6	43.89	0.290	8.6	0.60	6.8
	2.3	41.90	0.289	7.8	0.56	6.7
	2.2	42.60	0.283	7.3	0.60	7.1
	2.3	43.89	0.303	7.8	0.55	6.3
				average 8.4 ± 0.7		k_1 (average) 6.6 ± 0.3

[a] From pseudo-second-order plots of $1/[Co(CN)_5^{3-}]$ against time. [b] $k = k_{obs.}[Co(CN)_5^{3-}]_0/2[RX]$. [c] Initial rates from pseudo-first-order plots of log $[Co(CN)_5^{3-}]$ against time. [d] $k'_1 = k_i/2[RX]$. These values are in close agreement with k_1 values given in Table 2.

reverse step is in operation as shown in equation (4), being followed by a further reaction with $Co(CN)_5^{3-}$.

$$-d[Co(CN)_5^{3-}]/dt = 2k_1[Co(CN)_5^{3-}][RX] \qquad (3)$$

The presence of acrylonitrile, an efficient trap[9] for the radical R•, serves to remove R• as it is formed, eliminating the reverse k_{-1} step, thus rendering the rate-determining step as k_1, the values of which are given in Table 2. Average k_1 values of $(24.7 \pm 2.4) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and $(7.48 \pm 0.58) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} were found for 1-adamantyl iodide and 2,4-dimethyl-1-bicyclo[2.2.2]octyl iodide, respectively. These values are in close agreement with k'_1 values derived from initial rates k_i obtained from $\log[Co(CN)_5^{3-}]$ against time plots

$$Co(CN)_5^{3-} + RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R\cdot + Co(CN)_5X^{3-} \qquad (4)$$

of runs in the absence of acrylonitrile given in Table 1. This result lends support to the involvement of reaction (4). Since initially $[Co(CN)_5X^{3-}]$ is negligible, the contribution from the k_{-1} step will be so small that k'_1 derived from the initial rate k_i will approximate to k_1.

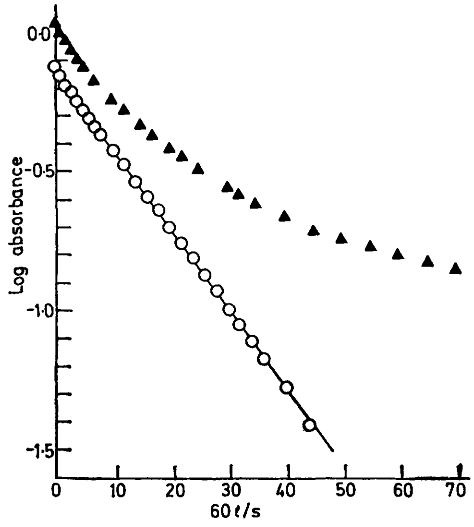

FIGURE 1 Plot of log absorbance of $Co(CN)_5^{3-}$ against time for the reaction with 1-adamantyl iodide: in the absence of acrylonitrile (▲) and in the presence of acrylonitrile (○) at 25 °C

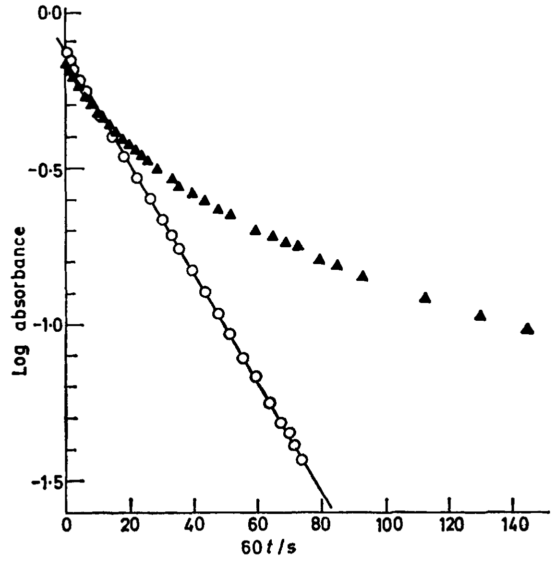

FIGURE 2 Plot of log absorbance of $Co(CN)_5^{3-}$ against time for the reaction with 2,4-dimethyl-1-bicyclo[2.2.2]octyl iodide: in the absence of acrylonitrile (▲) and in the presence of acrylonitrile (○) at 25 °C

The operation of the reverse step k_{-1} is further supported by the observed effect of added $K_3[Co(CN)_5I]$ on the second-order rate constants of the reaction of 1-adamantyl iodide. Because $K_3[Co(CN)_5I]$ was difficult to isolate in a pure state owing to ready hydrolysis,[10] it was prepared *in situ* immediately before use from the reaction of $[Co(NH_3)_5I]Cl_2$ and K[CN]. The results in the presence of 5.1 and 8.8 molar excesses of $K_3[Co(CN)_5I]$ over $Co(CN)_5^{3-}$ are given in Table 3. It will be observed that rate retardations of 35% and 82% were obtained respectively. It is also shown that these rate suppressions are not due to changes in ionic strength caused by the presence of $[NH_4][OH]$ and KCl produced by the reaction of $[Co(NH_3)_5I]Cl_2$ with K[CN], because two runs performed in the absence and presence of adjusted amounts of $[NH_4][OH]$ and KCl gave identical rate constants within the limits of experimental error. While these results can be explained qualitatively, it may be noted that rate suppressions will be affected by the loss of $Co(CN)_5I^{3-}$ due to $Co(CN)_5^{3-}$-catalysed and uncatalysed hydrolysis.[10] Furthermore, reaction (1) very likely produces R· and $Co(CN)_5I^{3-}$ in a solvent cage which would limit the effectiveness of added $Co(CN)_5I^{3-}$.

TABLE 2

Kinetic data for the reaction of 1-adamantyl iodide and 2,4-dimethyl-1-bicyclo[2.2.2]octyl iodide in the presence of acrylonitrile (0.10—0.11 mol dm^{-3}) at 25 °C

Organic halide, RX	[RX]/ 10^{-3} mol dm^{-3}	$10^3\ k'_{obs.}$/ s^{-1} [a]	$10^3\ k_1$/ dm^{-3} mol^{-1} s^{-1} [b]
(1) 1-(Adamantyl iodide	6.96	0.30	21.5
	10.35	0.53	25.6
	17.82	1.01	28.3
	21.0	1.09	26.0
	26.1	1.14	21.8
	28.3	1.42	25.1
			k_1 (average) 24.7 ± 2.4
(2) 1-Bicyclo-octyl iodide	14.96	0.20	6.68
	29.28	0.47	8.02
	43.90	0.68	7.74
			k_1 (average) 7.48 ± 0.58

[a] From the slopes of pseudo-first-order plots of log$[Co(CN)_5^{3-}]$ against time. [b] $k_1 = k'_{obs.}/2[RX]$.

TABLE 3

Effect of added $K_3[Co(CN)_5I]$ on the second-order rate constants for the reaction of 1-adamantyl iodide at 25 °C in 75% methanol

Run	Initial reactant concentration/10^{-3} mol dm^{-3}		$[Co(CN)_5I^{3-}]$/	
	$[Co(CN)_5^{3-}]$	[RX]	$[Co(CN)_5^{3-}]$	$k_{obs.}$/dm^3 mol^{-1} s^{-1}
1	0.57	7.68	0	1.18
2	0.59	7.68	0	1.22 [a]
3	0.63	7.68	5.1	0.80 [b]
4	0.86	7.75	8.8	0.20

[a] In the presence of added $[NH_4][OH]$, 0.016 mol dm^{-3}, and KCl, 0.0065 mol dm^{-3}, to simulate ionic strength due to $[NH_4][OH]$ and KCl in run 3. [b] $[K_3Co(CN)_5I]$ = 3.21 × 10^{-3} mol dm^{-3}.

As evident from the above discussion it is not necessary to invoke a new mechanism for the reaction of RX and $Co(CN)_5^{3-}$. Rather, the reaction with less reactive bridgehead iodides may represent limiting cases where k_1 is not simply the rate-limiting step. This may also be the case for other less reactive organic halides, for instance the vinyl and pyridyl iodides whose kinetic behaviour was reported [8] to be not fully established.

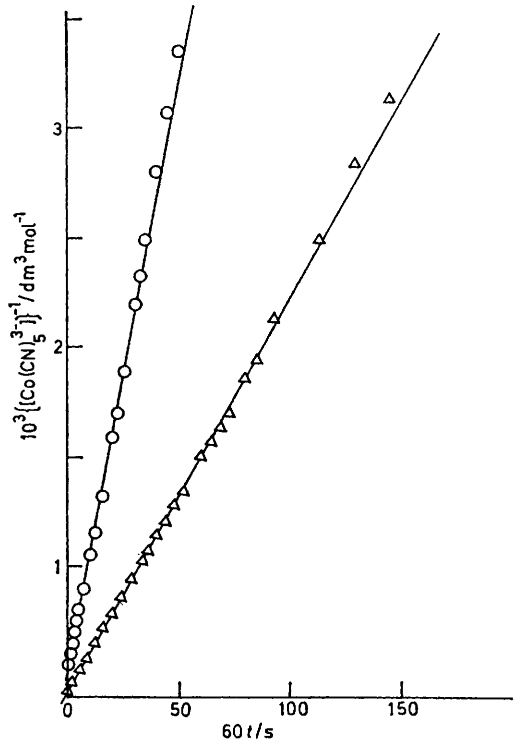

FIGURE 3 Plot of $1/[Co(CN)_5^{3-}]$ against time for the reaction in the absence of acrylonitrile of 2,4-dimethyl-1-bicyclo[2.2.2]-octyl iodide (43.89 × 10^{-3} mol dm^{-3}) with $Co(CN)_5^{3-}$ (2.3 × 10^{-3} mol dm^{-3}) (△) and 1-adamantyl iodide (21.45 × 10^{-3} mol dm^{-3}) with $Co(CN)_5^{3-}$ (1.8 × 10^{-3} mol dm^{-3}) (○)

The iodides (3), (4), and (5) were examined and found to be extremely low in reactivity. This, coupled with the limitations of their low maximum solubility in 80% methanol and the ready decomposition of $Co(CN)_5^{3-}$ at concentrations >0.1 mol dm^{-3} over long periods of time, gave immeasurably slow rates. The reaction of apocamphyl iodide (3) for example was estimated by monitoring of the organic halide by gas chromatography while keeping $[Co(CN)_5^{3-}]$ approximately con-

TABLE 4

A comparison of second-order rate constants for the reactions of $Co(CN)_5^{3-}$ with various organic iodides

	θ_c/°C	k/dm^3 mol^{-1} s^{-1}	Ref.
CH_3I	25.0	0.95 × 10^{-2}	8
$CH_3CH_2CH_2I$	25.0	4.3 × 10^{-2}	8
$(CH_3)_2CHI$	25.0	1.20	8
$(CH_3)_3CI$	25.0	9.1	8
(1) 1-Adamantyl iodide	25	2.47 × 10^{-2} *	This work
(2) 2,4-Dimethyl-1-bicyclo-[2.2.2]octyl) iodide	25	7.5 × 10^{-3} *	This work
(3) 7,7-Dimethyl-1-bicyclo-[2.2.1]heptyl) iodide	28	$<10^{-6}$	This work
(4) and (5) 9-Triptycyl iodide	28	$<10^{-6}$	This work

* Average from runs in Table 2, in the presence of acrylonitrile.

stant. The upper limit of this rate estimate is given in Table 4.

A comparison of the rates of reactions given in Table 4 shows that the reactivity of the bridgehead halides is very much reduced in comparison with normal halides, the tertiary 1-adamantyl iodide having reactivity only comparable to that of methyl and n-propyl iodides. The bridgehead bicyclo[2.2.2] iodide appears to be the limit for kinetic measurements and other more strained, or hindered systems are unlikely to react. The data obtained also reflect the stability of the bridgehead radicals and a comparison is made in Table 5. There is a marked parallel between the reactivity order obtained and that of the study of relative radical stability in the decarbonylation of bridgehead aldehydes by Applequist and Kaplan.[11] It may be noted that the adamantyl radical is generally believed to be less stable than the t-butyl radical.[2] Studies by Rüchardt [12] from competitive reactions of radicals from t-butyl peresters with carbon tetrachloride and bromotrichloromethane also revealed a similar pattern of radical reactivity for bridgehead radicals. Likewise, a different kinetic study of the thermal decomposition of peresters RCO_2OBu^t has also provided comparable results [13] as shown in Table 5.

TABLE 5

Relative reactivities

R	Relative reactivity of RX[a] with $Co(CN)_5^{3-}$	Relative stability of bridgehead radicals[b]	Relative rates[c]	Relative rates[d]
CH_3	3.8×10^{-1}			1.6×10^{-4}
$CH_3CH_2CH_2$	1.7	4.4×10^{-3}		
$(CH_3)_2CH$	4.9×10	3.7×10^{-2}		
$(CH_3)_3C$	3.7×10^{2}	4.0×10^{-1}		7×10^{-1}
1-Adamantyl	(1)	(1)	(1)	(1)
1-Bicyclo[2.2.2]octyl		4.8×10^{-1}	7.0×10^{-2}	1.1×10^{-1}
Dimethyl-1-bicyclo[2.2.2]octyl	3.0×10^{-1}			
1-Bicyclo[2.2.1]heptyl		2.8×10^{-3}	1.1×10^{-3}	1.0×10^{-3}
Dimethyl-1-bicyclo[2.2.1]heptyl	$<10^{-4}$			
9-Triptycyl	$<10^{-4}$		7.4×10^{-4}	

[a] RX is the organic iodide in all cases. [b] Ref. 11. [c] Ref. 12. [d] Ref. 13.

EXPERIMENTAL

Cobalt(II) chloride and potassium cyanide were Hopkin and Williams AnalaR grade. The compound $[Co(NH_3)_5I]Cl_2$ was prepared according to reported procedures.[14] Methanol was B.D.H. AnalaR grade. Other reagent-grade chemicals were from Fluka.

The n.m.r., i.r., and u.v. spectra were recorded on Hitachi–Perkin-Elmer R20B, Hilger and Watts Infrascan, and Unicam SP700 instruments respectively. Gas chromatography (g.c.) was performed on a Varian Aerograph Series 1800 instrument using a 1.5 m 10% SE-30 column. Mass spectra (m.s.) and g.c.–m.s. were performed on a AEI MS30 mass spectrometer with a DS50 data system.

Syntheses of Organic Halides.—*1-Adamantyl iodide* (1) was prepared as described in the literature.[15] *2,4-Dimethyl-1-bicyclo*[2.2.2]*octyl iodide* (2) was prepared as described in an earlier paper.[6] *9-Triptycyl iodide* (9,10-dihydro-9,10-*o*-benzeno-9-anthracenyl iodide) (4) was synthesised from 9-anthracenyl iodide and anthranilic acid by a Diels–Alder reaction according to reported procedures.[16] Similarly (5) was prepared from 9-anthracenyl iodide and maleic anhydride.

1-Apocamphyl bromide (7,7-dimethyl-1-norbornyl bromide) was prepared from D,L-10-camphorsulphonic acid according to reported procedures.[17-20] The bromide was finally converted to 1-apocamphyl iodide (3) by halogen exchange [21] as follows.

To 1-apocamphyl bromide (3.45 g, 17 mmol) in methyl iodide (30 cm^3) in the presence of aluminium foil (1.54 g, 57 mmol) in a flask equipped with a reflux condenser under dry nitrogen, was added bromine (1.92 g, 12 mmol). Heat was evolved and the reaction mixture refluxed without any heat supply for the initial 30 min. As the evolution of heat subsided, the reaction mixture was heated under reflux (42 °C) for a further 3.5 h. The reaction mixture was cooled in an ice bath and water added dropwise. Vigorous reaction ensued until *ca.* 1 cm^3 H_2O had been added. A further 30 cm^3 of water was added and the methyl iodide layer separated. This was washed till a clear aqueous layer was obtained, followed by 10% sodium thiosulphate and finally water. The methyl iodide solution was dried ($Mg[SO_4]$). Removal of methyl iodide *in vacuo* gave a pale yellow solid, 3.97 g (15.9 mmol, 92% yield). Recrystallisation from hexane gave colourless needles, m.p. 132—133 °C; mass spectrum M^+ 250.021 4 (calc. for $C_9H_{15}I$, 250.022 0); $\tau(CDCl_3)$ 9.03 (s, 6 H, 2 Me) and 7.45—8.85 (m, 9 H).

Kinetic Measurements.—Solutions of 1-adamantyl iodide in methanol were found to deteriorate rapidly when left exposed to light at room temperature and hence must be prepared just before the kinetic runs.

In a typical run with 1-adamantyl iodide, the crystalline solid iodide was weighed directly into a 1-cm or 2-cm cell and dissolved in a definite volume of methanol under N_2. In some runs, acrylonitrile (20 μl in a 1-cm cell or 40 μl in in 2-cm cell) was added. A 0.1 mol dm^{-3} aqueous solution of cobalt(II) chloride (60—100 μl) was injected into the cell, followed by an appropriate volume of water to achieve a final composition of 80% methanol to 20% water (v/v) for the reaction. After thermostatting to 25 ± 0.5 °C the reaction was initiated by the injection of an aqueous 1.2 mol dm^{-3} solution of K[CN] (50—90 μl), and followed by monitoring the concentration of $Co(CN)_5^{3-}$ at 980 nm ($\varepsilon_{max.}$ 298).[22] Runs were also performed in the presence of $K_3[Co(CN)_5I]$ in a 4-cm cell, with $K_3[Co(CN)_5I]$ added as a 0.05—0.10 mol dm^{-3} aqueous solution, prepared immediately before use by the reaction of an aqueous suspension of $[Co(NH_3)_5I]Cl_2$ with a five-fold molar excess of K[CN]. The solvent medium was adjusted to 75% methanol, and as described above, the reaction was finally initiated by the injection of K[CN].

In runs with 2,4-dimethyl-1-bicyclo[2.2.2]octyl iodide, appropriate volumes of a 0.05 mol dm^{-3} methanolic solution of iodide, acrylonitrile (20—40 μl), 0.1 mol dm^{-3} aqueous cobalt(II) chloride (60—100 μl) were injected into a 1-cm or 2-cm cell under N_2 followed by water to achieve a final solvent composition of 80% methanol to 20% water (v/v). The cell was thermostatted to 25 ± 0.5 °C, and the reaction initiated by the injection of 1.2 mol dm^{-3} K[CN] (30—50 μl). The concentration of $Co(CN)_5^{3-}$ was followed at 980 nm.

With both 1-adamantyl iodide and 2,4-dimethyl-1-bicyclo[2.2.2]octyl iodide linear plots were obtained for $1/[Co(CN)_5^{3-}]$ against time in the absence of acrylonitrile and $\log[Co(CN)_5^{3-}]$ against time in the presence of acrylonitrile. Typical plots are shown in Figures 1—3. The respective second- and first-order rate constants obtained from the slopes of these linear plots are given in Tables 1 and 2. Initial first-order rate constants were also estimated for runs in the absence of acrylonitrile, from their non-linear $\log[Co(CN)_5^{3-}]$ against time plots. These are also listed in Table 1.

The reaction of 1-apocamphyl iodide (0.018 mol dm^{-3}) and $Co(CN)_5^{3-}$ (0.036 mol dm^{-3}) in 80% methanol was followed at 28 °C under nitrogen. The concentrations of the reactants in this reaction were limited by the low solubility of the organic iodide in aqueous methanolic solutions. The reaction was monitored both by the decrease of $Co(CN)_5^{3-}$ as above, and by the change in the concentration of apocamphyl iodide as determined by quantitative g.c. analyses of aliquots over four days during which the concentration of $Co(CN)_5^{3-}$ was kept approximately constant.

The reactions of 9-triptycyl iodide and the related Diels–Alder adduct (5) were similarly followed.

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