Substitution in Bis-(2,2′-bipyridyl)biscyanoiron(II) in Aqueous Ethanol

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Summary The mechanism of substitution for the uncharged complex [Fe bipy$_2$(CN)$_2$]^0 has been investigated by the Grunwald–Winstein method of determining the solvent variation of rate constant.

THE role of water in transition state formation for aquation of octahedral complexes continues to be a matter for discussion. One way of examining this role is to apply the Grunwald–Winstein[1] treatment of dependence of reaction rate on solvent properties, which has been widely used in organic chemistry, to this problem. This approach has been tried, but its validity in these earlier cases[2,3] is open to some question since the complexes involved were charged ions rather than neutral molecules. We now report kinetic results for substitution of the 2,2′-bipyridyl ligand in the zero-charged complex bis-(2,2′-bipyridyl)biscyanoiron(II), [Fe bipy$_2$(CN)$_2$]^0, by 1,10-phenanthroline. In this system all reactants and products are uncharged species, so the Grunwald–Winstein treatment can be used without the introduction of further assumptions or modifications.

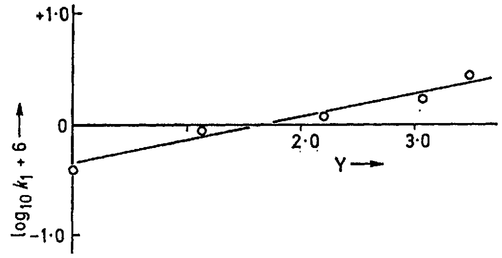

FIGURE. *Correlation of logarithms of first-order rate constants* (k$_1$) *for substitution at* [Fe bipy$_2$(CN)$_2$]^0 *with solvent* Y *values.*

Kinetics were followed spectrophotometrically at 35·0° in the thermostatted cell compartment of a Unicam SP800A recording spectrophotometer. First-order kinetics were closely followed; graphically determined first-order rate constants are reported in the Table. Decadic logarithms of these rate constants correlate with Grunwald–Winstein solvent Y values (see Figure). The slope of this correlation graph is 0·2. This is far from the value of 1·0 expected for an S_N1 (lim) mechanism, but is rather in the region expected for S_N2 hydrolysis [*cf.* the value of 0·3 for S_N2 hydrolysis of (Me$_2$N)$_2$POCl[4]]. In view of the π-withdrawing properties of cyanide ligands this is not too surprising. It would now be interesting to extend this investigation to uncharged cobalt(III)–ammine complexes, whose mechanism of substitution is generally considered to be primarily dissociative.

Average first-order constants for substitution of bis-(2,2′*-bipyridyl*)*-biscyanoiron*(II), *initial concentration* 1·8 × 10^{-4} M, *by* 1,10-*phenanthroline, initial concentration* 4·1 or 8·2 × 10^{-3} M, *in aqueous ethanol at* 35·0°. *Solvent* Y*-values are taken from reference* 1

% EtOH v/v	Y	$10^6 k_1$ (sec.$^{-1}$)
0	3·49	(2·8)*
20	3·05	1·6
40	2·20	1·1
60	1·12	0·9
80	0	0·4

* Approximate value; product very sparingly soluble.

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