The Pentacyanonitrosylferrate Ion. Part 2.† Reactions with Various Carbanions

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The carbanions of malononitrile, ethylmalononitrile, and dimethyl malonate react with pentacyanonitrosylferrate (nitroprusside) to form highly coloured adducts. A kinetic study has shown that, in the second and third cases, there is rate-determining reaction between carbanion and nitroprusside but, in the first, the product is that formed by a second ionisation to give $[Fe(CN)_5N(O)C(CN)_2]^{4-}$.

In the pentacyanonitrosylferrate (nitroprusside) ion the nitrosyl ligand is present[1] as NO^+. This makes it susceptible to attack by nucleophiles and we have recently reported[2] a study of its reaction with amines. Carbanions also react and the initial product is a fairly stable, highly coloured adduct.[3] Reaction is fast but reaction rates may be measured by stopped-flow spectrophotometry.

Colours resulting from addition of carbon acids to alkaline solutions of nitroprusside were first reported many years ago[4] and the reaction is sometimes known as the Légal reaction.[5] More recently the reactions between ketones and alkaline nitroprusside were studied by Loach and Turney[6] and by Swinehart and Schmidt.[7] From the latter study it was concluded, without direct kinetic evidence, that, for reaction with acetone, the rate-determining step is attack on nitroprusside by the carbanion. We have examined the reactions of stronger carbon acids than that chosen by Swinehart and Schmidt[7] and now report our results.

Mechanism 1: slow deprotonation of the adduct

$$\underset{(1)}{[Fe(CN)_5NO]^{2-}} + {}^-CH(CN)_2 \overset{K_2}{\rightleftharpoons} \underset{(2)}{[Fe(CN)_5N(O)CH(CN)_2]^{3-}}$$

$$(2) + HO^- \xrightarrow[\text{slow}]{k} \underset{(3)}{[Fe(CN)_5N(O)C(CN)_2]^{4-}} + H_2O$$

Scheme 1.

Mechanism 2: adduct formation from a doubly charged carbanion

$${}^-CH(CN)_2 + HO^- \overset{K_3}{\rightleftharpoons} {}^{2-}C(CN)_2 + H_2O$$

$$\underset{(1)}{[Fe(CN)_5NO]^{2-}} + {}^{2-}C(CN) \xrightarrow[\text{slow}]{k} \underset{(3)}{[Fe(CN)_5N(O)C(CN)_2]^{4-}}$$

Scheme 2.

Results and Discussion

The first carbon acid selected for study was malononitrile. As hydroxide reacts quite rapidly with nitroprusside,[7] and as alkaline solutions of malononitrile are unstable, rather dilute NaOH solutions were used. These solutions were placed in one arm of the stopped-flow mixing device, and aqueous mixture of sodium nitroprusside and an excess (to give first-order conditions) of malononitrile in the other. On mixing there was a rapid increase in absorbance at 500 nm; the coloured product was sufficiently stable on the stopped-flow time-scale to permit determination of its rate of formation as a function of reactant concentrations. A few experiments were performed in which the carbanion was preformed; this resulted in no change in the kinetics and so clearly carbanion formation is not the rate-determining step. The concentrations of malononitrile and hydroxide were such that ionisation of the acid was substantial but incomplete. In each case the equilibrium carbanion concentration, in excess over that of nitroprusside, was calculated from the known pK_a (11.39)[8] of malononitrile. Data for a number of runs are displayed in the Table. It is clear that the observed first-order rate constant is not directly proportional to the equilibrium carbanion concentration, as would be the case if the mechanism were rate-determining reaction between carbanion and nitroprusside. The rate of adduct formation depends also upon the equilibrium hydroxide concentration ($[HO^-]_e$). This can be explained in at least two ways, both of which involve production of a deprotonated adduct (3), and it is the formation of this species which has been observed. If we assume that slow step is the second ionisation, then $d[(3)]/dt = k[(2)][HO^-]_e$. If (2) is present at a low steady-state then $d[(3)]/dt = -d[(1)]/dt$ and $k_{obs} = kK_2[{}^-CH(CN)_2]_e[HO^-]_e$.

If we assume that reaction with ${}^{2-}C(CN)_2$ is the slow step then $d[(3)]/dt = k[(1)][{}^{2-}C(CN)_2]_e$. The term $[{}^{2-}C(CN)_2]_e$ is $K_3[{}^-CH(CN)_2]_e[HO^-]_e$ and it is assumed to be present at low steady-state, so that $k_{obs} = kK_3[{}^-CH(CN)_2]_e[HO^-]_e$. Thus, for both mechanisms 1 and 2, a plot of k_{obs} *vs.* $[{}^-CH(CN)_2]_e[HO^-]_e$ should be rectilinear through the origin. This is indeed the case (Figure 1). The kinetic data are consistent with both mechanisms but do not allow us to distinguish between them.

Formation of a doubly charge carbanion appears, at first sight, to be rather unlikely, but the charge is substantially delocalised over the two cyano groups and so the situation does not represent a concentration of negative charge on a single carbon atom. Mechanism 2 means, also, that removal of a proton from ${}^-CH(CN)_2$ must be faster than reaction of ${}^{2-}C(CN)_2$ with nitroprusside. However, the latter reaction is between two doubly negatively charged species and so may well be rather slow. Its irreversibility is not surprising as in (3) there is the possibility of extensive delocalisation of charge over seven cyano-groups, giving the species a stability greater than that of a carbanion. Further discussion of distinguishing between mechanism 1 and 2 will be delayed until the reactions of ethylmalononitrile have been considered.

An attempt to isolate the adduct formed by reaction of malononitrile and nitroprusside gave a dark red powder. Attempts to purify this material resulted in its decomposition and so it was submitted for analysis in the state in which it came out of solution. The results were indicative rather than diagnostic. It is very probable that water of crystallisation is present and if we assume the formula $Na_4[Fe(CN)_5NOC$-

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† Part 1, ref. 2.

Table. Kinetic data for the reaction of nitroprusside with the carbanion of malononitrile at 25 °C

	$10^2[CH_2(CN)_2]_t{}^a$/M	$10^2[HO^-]_t{}^b$/M	$10^2[^-CH(CN)_2]_e{}^c$/M	k_{obs}/s^{-1}
(a)	1.01	1.00	0.589	1.20
	1.01	2.00	0.806	4.40
	1.01	3.00	0.882	8.60
	1.01	4.00	0.917	14.8
	1.01	5.00	0.937	22.8
(b)	2.00	1.00	0.803	1.00
	2.00	2.00	1.37	4.20
	2.00	3.00	1.64	9.80
	2.00	4.00	1.77	18.9
	2.00	5.00	1.83	27.9
(c)	3.01	1.00	0.879	1.14
	3.01	2.00	1.65	3.63
	3.01	3.00	2.22	9.12
	3.01	4.00	2.51	17.5
	3.01	5.00	2.67	29.8
(d)	4.10	1.00	0.915	0.75
	4.10	2.00	1.78	3.10
	4.10	3.00	2.53	7.20
	4.10	4.00	3.10	15.7
	4.10	5.00	3.45	27.4

[a] Stoicheiometric concentration of malononitrile. [b] Stoicheiometric concentration of hydroxide. [c] Equilibrium concentration of malononitrile carbanion.

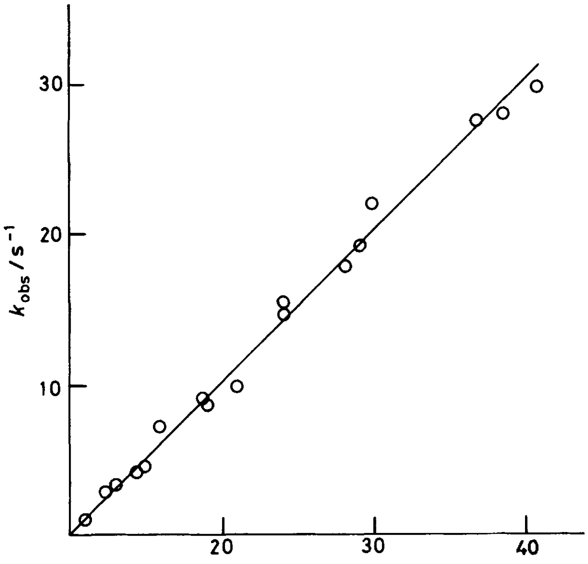

Figure 1. Kinetic data for the reaction of nitroprusside with the carbanion of malononitrile; $[\text{nitroprusside}]_0 = 10^{-3}$M, $I = 0.1$M

$(CN)_2]\cdot 3.5H_2O$ then the agreement between theory and experiment (experimental values in parentheses) is reasonable: C, 22.0 (21.4); N, 25.7 (25.1); H, 1.6 (1.6); Na, 21.1 (19.2); Fe, 12.9 (13.4)%.

A second ionisation is not possible with ethylmalononitrile (**4**) and, if either mechanism for malononitrile is correct, different kinetics for its reaction with alkaline nitroprusside should be observed. A similar colour developed on mixing but it was much less intense. The rate of formation was measured with a stopped-flow spectrophotometer in the same manner as for the reaction of malononitrile. Equilibrium carbanion concentrations were calculated using a pK_a value of 12.84.[8] In this case a plot of k_{obs} *vs.* equilibrium carbanion concentration was rectilinear through the origin (Figure 2) and the value of k_{obs} was unaffected by the equilibrium concentration of hydroxide. We propose the mechanism shown in Scheme 3. Subsequent fading of the solution was too fast to permit isolation of the adduct.

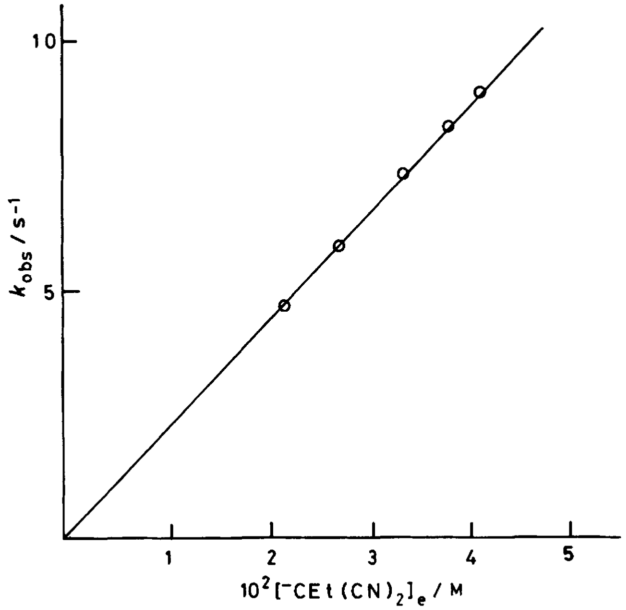

Figure 2. Kinetic data for the reaction of nitroprusside with the carbanion of ethylmalononitrile; $[\text{nitroprusside}]_0 = 2.3 \times 10^{-3}$M, $I = 0.25$M

The kinetic evidence for reaction of ethylmalononitrile points unambiguously to rate-determining reaction between nitro-

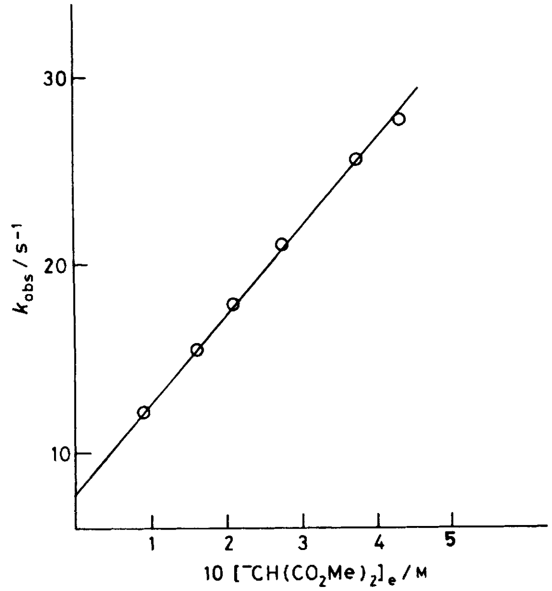

Figure 3. Kinetic data for the reaction of nitroprusside with the carbanion of dimethyl malonate; $[\text{nitroprusside}]_0 = 1.4 \times 10^{-3}$M, I = 0.25M

$$\underset{(4)}{CHEt(CN)_2} + HO^- \xrightleftharpoons{K_1} {}^-CEt(CN)_2 + H_2O$$

$${}^-CEt(CN)_2 + [Fe(CN)_5NO]^{2-} \xrightarrow{k} \underset{(5)}{[Fe(CN)_5N(O)CEt(CN)_2]^{3-}}$$

Scheme 3.

prusside and a carbanion, a reaction which is irreversible. This is not the case in Scheme 1 and it is difficult to see why the replacement of an ethyl group by a hydrogen atom should change K_2 so much that (**2**) forms to only a small extent, *i.e.* the decomposition of (**2**) is fast, while that of (**5**) in Scheme 3 is too small to be measured. This analysis suggests that mechanism 2 is correct for malononitrile, where the rate-determining step is again reaction between nitroprusside and a carbanion. However, mechanism 2 is not without difficulties. For formation of (**3**), rather than (**2**), to be the predominant reaction it must be that deprotonation of $^-CH(CN)_2$ is fast in comparison with the reaction of $^-CH(CN)_2$ with nitroprusside. The kinetic evidence persuades us that this is the case.

Dimethyl malonate (**6**) is a much weaker acid than malononitrile and so a second ionisation is unlikely. Thus, the kinetics of reaction of (**6**) with nitroprusside should be different from those of malononitrile. On mixing, a similar colour developed but it was, again, less intense. The value of k_{obs}, determined by stopped-flow spectrophotometry, showed no dependence on $[HO^-]_e$. The equilibrium carbanion concentration was calculated assuming that the pK_a of dimethyl malonate is the same as that of diethyl malonate (13.3).[9] A plot of k_{obs} *vs.* carbanion concentration is rectilinear (Figure 3), with a positive intercept. We therefore propose the mechanism shown in Scheme 4. The second process must, in this case, be an equilibrium, to explain the positive intercept. The colour faded too quickly to permit isolation of the adduct.

The fact that the reaction between nitroprusside and carbanion is, in this case, an equilibrium requires comment. Steric factors have a considerable effect on the reactions of nitro-

$$\underset{(6)}{CH_2(CO_2Me)_2} + HO^- \xrightleftharpoons{K_1} {}^-CH(CO_2Me)_2 + H_2O$$

$${}^-CH(CO_2Me)_2 + [Fe(CN)_5NO]^{2-} \rightleftharpoons [Fe(CN)_5N(O)CH(CO_2Me)_2]^{3-}$$

Scheme 4.

prusside. For example, the anion of Meldrum's Acid does not react with nitroprusside at all.[10] It is reasonable, then, that the bulky nature of dimethyl malonate should disfavour adduct formation but enhance its dissociation, and so what appears to be an irreversible reaction with malononitrile and ethylmalononitrile is a detectable equilibrium in this instance.

This study exemplifies the way in which electron-withdrawing ligands like cyanide can delocalise charge to such an extent that reactions between two negatively charged species can occur readily.

Experimental

Reagents were AnalaR where available. Sodium nitroprusside solutions were carefully protected from light by the use of aluminium foil. Ethylmalononitrile was prepared from diethyl ethylmalonate by conversion into the diamide[11] and subsequent reaction with $POCl_3$.[12] The crude product was distilled twice *in vacuo* to give a colourless liquid, b.p. 92 °C at 19 mmHg (lit.,[8] 90—91 °C at 20 mmHg).

Rate constants were measured by the use of a Canterbury SF-3A stopped-flow spectrophotometer connected to a Commodore 4016 microcomputer *via* a transient recorder. For malononitrile the computer program calculated first-order rate constants using infinity values; for the other carbon acids, a program using the Kezdy–Swinbourne method was used, as the colour faded very rapidly. Correlation coefficients were always better than 0.99. The ionic strength was maintained at 0.1M or 0.25M by addition of KCl. All rate constants were measured at 25 °C.

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