Nitrosation of Meldrum's Acid (2,2-Dimethyl-1,3-dioxane-4,6-dione) and Ethyl Acetoacetate

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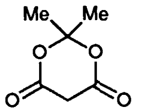
At low acidity (below *ca.* 0.1 mol dm^{-3}), nitrosation of Meldrum's acid in water takes place *via* the carbanion (or enolate), both for reactions of $H_2NO_2^+/NO^+$ and XNO species [X = Cl, Br, SCN and $^+SC(NH_2)_2$], whereas at higher acidities another pathway takes over involving reaction *via* the enol tautomer. These two pathways have been clearly identified kinetically by different dependencies of their rate constants upon the acidity of the solution. In neither case is the ionisation to the carbanion or the enolisation rate-limiting. The carbanion is, as expected, much more reactive than is the enol, and some of its reactions occur at the encounter limit. In contrast, the less acidic ethyl acetoacetate reacts entirely *via* the enol form, under all conditions. The results from both substrates are compared and discussed, together with other published results in this area.

2,2-Dimethyl-1,3-dioxane-4,6-dione **I** or Meldrum's Acid (referred to henceforth as MH) is a member of a family of cyclic 1,3-diones which also includes dimedone **II** and barbituric acid **III**. The unusual feature of Meldrum's Acid is its high acidity (pK_a 4.83[1]). This has been described recently[2] in terms of 'one of the largest stereoelectronic effects in the literature of organic chemistry.' This statement has prompted a number of theoretical investigations into the reason(s) for this high acidity.[3] Whatever the cause, it means that MH is susceptible to electrophilic attack at the carbanionic site, at position 5 in the molecule. Indeed the chemistry of MH is dominated by these reactions together with those of nucleophilic attack at the carbonyl carbon atoms.[4] Halogenation yields mono- or di-substitution products[5] and there are two literature references[6] to the isolation of an unstable oxime by reaction with sodium nitrite in water (Scheme 1). MH itself exists primarily in the diketo form, with a very small enol content (K_E 4.05 × 10^{-3})[7] (Scheme 2). This contrasts quite markedly with the behaviour of dimedone which exists in aqueous solution primarily as the enol tautomer.[8]



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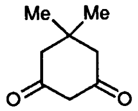

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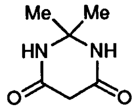

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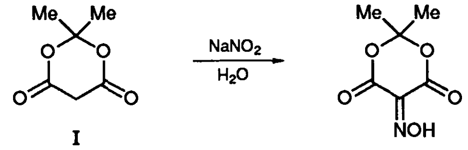
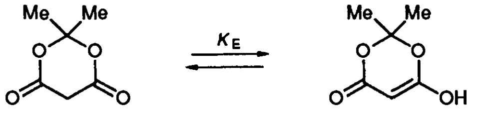


Scheme 1



I

Scheme 2

The possibility then exists that electrophilic attack in MH can occur either *via* the carbanion (enolate) or the enol intermediates. It has been established that nitrosation of simple ketones (such as acetone) takes place *via* the enol forms.[9] In this work we have examined mechanistically the nitrosation of MH together with, for comparison purposes, that of ethyl acetoacetate. Ethyl acetoacetate is a much weaker acid (pK_a 10.7) than is MH, and is well-known to exist in the enol form to an extent which is dependent on the nature of the solvent.

Experimental

MH was purified by recrystallisation according to a literature procedure,[10] and ethyl acetoacetate (EAA) by distillation under reduced pressure. All other reagents were of the highest purity grade available. Stock solutions of sodium nitrite were made up daily as required. Kinetic measurements were carried out in water at 25 °C either in a conventional UV spectrophotometer or for the fast reactions, in a stopped-flow UV spectrophotometer. Reactions were monitored either at λ = 245 or 320 nm for MH, noting the increasing absorbance due to the product oxime, and at 370 nm for EAA noting the decreasing absorbance due to nitrous acid. The solvent for the reactions of EAA contained 20% dioxane in water for solubility reasons. In all cases reactions were carried out with [MH] or [EAA] in at least a twenty-fold excess over the [HNO_2]. In general, good first order kinetic behaviour (with a reproducibility of ±5%) was found throughout except for some of the reactions of MH at intermediate acidity. We ascribe this latter effect to a subsequent reaction of the product oxime with nitrous acid (in some acid catalysed reactions), which is not a problem at low acidities nor when reactions are catalysed by halide ion *etc.* These experiments were analysed by the initial rate method (with an accuracy of *ca.* ±10%) and gave results which fitted in well with those found in other acid regions. MH is known to undergo hydrolysis reactions. These were found to be very slow under our experimental conditions and were not competitive with the nitrosation reactions.

Results and Discussion

Meldrum's Acid (MH).—(i) *Reactions at low acidity* (*below* ca. 0.1 mol dm^{-3}). Plots of the measured first order rate constant k_0 *vs.* $[MH]_0$ (with $[MH]_0 \gg [HNO_2]_0$) were all good straight lines with a small but significant intercept at $[MH]_0 = 0$. Fig. 1 shows the results for a typical set of data. This suggests that the overall reaction is reversible and k_0 is given by eqn. (1) where k_1

Table 1 Nitrosation of MH at different acidities, [MH] = 1.05×10^{-2} mol dm^{-3}, [HNO_2] = 1.45×10^{-4} mol dm^{-3} and constant ionic strength (0.5)

$[H^+]/10^{-2}$ mol dm^{-3}	$k_0/10^{-3}$ s^{-1}
1.2	3.2
1.8	3.3
2.4	3.1
3.0	2.8
3.6	2.8
4.2	2.7

Table 2 Cl^- and Br^- catalysis of the nitrosation of MH at low acidity at constant ionic strength (0.5)

$[Cl^-]$ or $[Br^-]$/ mol dm^{-3}	[MH]/mol dm^{-3}	$[H^+]$/mol dm^{-3}	k_0/s^{-1}
0.116 (Cl^-)	1.15×10^{-2}	1.94×10^{-2}	3.22×10^{-2}
0.232 (Cl^-)	1.15×10^{-2}	1.94×10^{-2}	6.05×10^{-2}
0.348 (Cl^-)	1.15×10^{-2}	1.94×10^{-2}	8.10×10^{-2}
0.464 (Cl^-)	1.15×10^{-2}	1.94×10^{-2}	10.2×10^{-2}
0.250 (Cl^-)	3.2×10^{-2}	0.116	0.158
0.250 (Cl^-)	3.2×10^{-2}	0.231	0.156
0.250 (Cl^-)	3.2×10^{-2}	0.345	0.158
0.040 (Br^-)	1.28×10^{-2}	1.94×10^{-2}	0.418
0.099 (Br^-)	1.28×10^{-2}	1.94×10^{-2}	0.991
0.198 (Br^-)	1.28×10^{-2}	1.94×10^{-2}	2.12
0.396 (Br^-)	1.28×10^{-2}	1.94×10^{-2}	4.29
0.495 (Br^-)	1.28×10^{-2}	1.94×10^{-2}	5.70
0.320 (Br^-)	2.8×10^{-3}	1.94×10^{-2}	1.10
0.320 (Br^-)	5.6×10^{-3}	1.94×10^{-2}	1.71
0.320 (Br^-)	8.4×10^{-3}	1.94×10^{-2}	2.24
0.320 (Br^-)	11.2×10^{-3}	1.94×10^{-2}	2.87
0.290 (Br^-)	1.18×10^{-2}	1.14×10^{-2}	3.60
0.290 (Br^-)	1.18×10^{-2}	2.28×10^{-2}	2.84
0.290 (Br^-)	1.18×10^{-2}	2.85×10^{-2}	3.21
0.290 (Br^-)	1.18×10^{-2}	4.00×10^{-2}	2.95

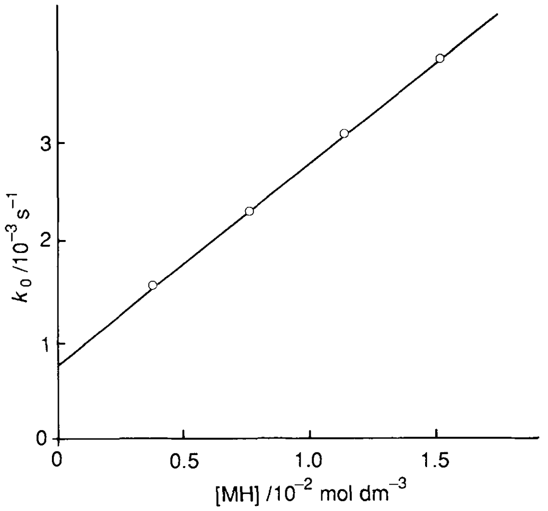


Fig. 1 Plot of k_0 *vs.* [MH] for the nitrosation of MH at 3.80×10^{-2} mol dm^{-3} $[H^+]$, 1.41×10^{-4} mol dm^{-3} [HNO_2], and I = 0.5 ($NaClO_4$)

$$k_0 = k_1[MH]_0 + k_{-1} \tag{1}$$

is the second order rate constant for the forward reaction and k_{-1} the first order rate constant for the reverse reaction. Values of the overall equilibrium constant K ($=k_1/k_{-1}$) were found to be 250 and 220 dm^3 mol^{-1} for two sets of measurements made at two different acidities and at constant ionic strength (I = 0.5). Thus oxime formation is very much favoured over the reverse reaction under our experimental conditions. Reversibility of nitrosation reactions is well known in some *N*-nitrosation reactions,[11] and has also recently been reported as a small effect for oxime formation from the nitrosation of malononitrile.[12] At low acidity the value of k_0 is unaffected by the acidity (see Table 1). This strongly suggests (since we are in the acid range where virtually all of the nitrite anion is protonated) that the reaction occurs *via* the carbanion, so that acid catalysis of nitrosation is balanced by the ionisation to the carbanion, as outlined in Scheme 3. The pattern of behaviour is thus similar to that of malononitrile which reacts at even lower acidities. The results yield an average value of 12 700 dm^6 mol^{-2} s^{-1} for the third order rate constant k_3 [defined by eqn. (2)] for the forward reaction. This value is remarkably close to values previously obtained for nitrosation of other negatively charged species under acid conditions at this temperature, *i.e.* 11 700 dm^6 mol^{-2} s^{-1} for reaction of the thiocyanate ion,[13] and 11 800 dm^6 mol^{-2} s^{-1} for the benzenesulphinate ion.[14] The value of *ca.* 12 000 dm^6 mol^{-2} s^{-1} is taken to be the encounter limit[15] for reaction between charged reactants of the opposite sign. In this case it is not possible to deduce the actual bimolecular rate constant, since K_{NO^+} is not known with any certainty.

$$MH \rightleftharpoons M^- + H^+ \; (K_a)$$

$$HNO_2 + H^+ \rightleftharpoons H_2NO_2^+ \text{ (or } NO^+ + H_2O) \; (K_{NO^+})$$

$$H_2NO_2^+ \text{ (or } NO^+) + M^- \rightleftharpoons \text{Oxime}$$

Scheme 3

$$\text{Rate} = k_3[M^-][HNO_2][H^+] \tag{2}$$

As expected, nitrosation of MH is markedly catalysed by both Cl^- and Br^-. Again the reactions are somewhat reversible and as before are independent of the acid concentration at low acidities. The data for the catalysed reactions are given in Table 2. Again these results accord with a reaction of the anion M^- with ClNO or BrNO. Throughout, the rate limiting step is attack of the nitrosating agent. It appears that under these conditions the rate of reprotonation of M^- (which must be encounter controlled) is much greater than the rate of XNO (or $H_2NO_2^+$) attack, for even if the latter is encounter controlled, the concentration of XNO (and $H_2NO_2^+$) is very much less than is the stoichiometric concentration of 'total nitrous acid', and so, much less than the $[H^+]$.

If the overall reversibility of the reaction is ignored, then the various results in Table 2 yield values of k_2 [defined by eqn. (3)]

$$\text{Rate} = k_2[XNO][M^-] = k_2K_{XNO}[X^-][HNO_2][MH]K_a \tag{3}$$

for the reaction of XNO and M^- as follows: 1.0×10^9 and 1.1×10^9 dm^3 mol^{-1} s^{-1} for ClNO and 1.1×10^9, 8.5×10^8 and 1.2×10^9 dm^3 mol^{-1} s^{-1} for BrNO respectively. When allowance is made for the overall reversibility of the reaction, these values are all reduced by about 20%. Another set of results showed k_0 to be effectively independent of the acidity up to *ca.* 0.3 mol dm^{-3} for both Cl^- and Br^- catalysed reactions and yielded further values of k_2 of 1.1×10^9 and 1.2×10^9 dm^3 mol^{-1} s^{-1} for ClNO and BrNO reactions respectively. It is clear that both reactions occur at a rate which is at, or close to, the encounter controlled limit. This is suggested by the very close similarity of the two reaction rate constants, given that for less reactive substrates ClNO is always more reactive than is BrNO. The actual values are a little lower than the calculated limiting value of 7×10^9 dm^3 mol^{-1} s^{-1}, but are considered to be sufficiently close given the assumptions made in the derivation of the limiting value. Thus the anion from Meldrum's Acid behaves much like the carbanion for malononitrile[12] in reaction with the two nitrosyl halides.

Table 3 SCN^- and $SC(NH_2)_2$ catalysis of MH nitrosation at low acidity. $[MH] = 8.25 \times 10^{-3}$, $[HNO_2] = 6.2 \times 10^{-3}$ mol dm^{-3}, I = 0.5.

$[SCN^-]$/ 10^{-3} mol dm^{-3}	$[SC(NH_2)_2]$/ 10^{-4} mol dm^{-3}	$[H^+]$/ 10^{-2} mol dm^{-3}	k_0/s^{-1}
1.5	—	4.4	0.84
1.5	—	7.5	1.01
1.5	—	11.1	1.18
1.5	—	14.2	1.35
—	3.96	4.4	0.42
—	3.96	9.0	0.65
—	3.96	17.5	1.14
—	3.96	26.5	1.54

Table 4 Acid catalysis in the nitrosation of MH at high acidity. $[MH] = 1.57 \times 10^{-2}$ mol dm^{-3}, $[HNO_2] = 1.1 \times 10^{-4}$ mol dm^{-3}.

$[H^+]$/mol dm^{-3}	$k_0/10^{-2}$ s^{-1}
1.52	0.96
2.09	1.33
2.66	1.64
3.04	2.01

Table 5 Second order rate constants (dm^3 mol^{-1} s^{-1}) for reaction of XNO with the enol and carbanion derived from Meldrum's Acid

XNO	Enol	Carbanion
ClNO	1.5×10^7	1.1×10^9
BrNO	1.4×10^7	1.1×10^9
NCSNO	3.2×10^6	1.1×10^8
$(NH_2)_2C\overset{+}{S}NO$	8.0×10^4	8.4×10^5

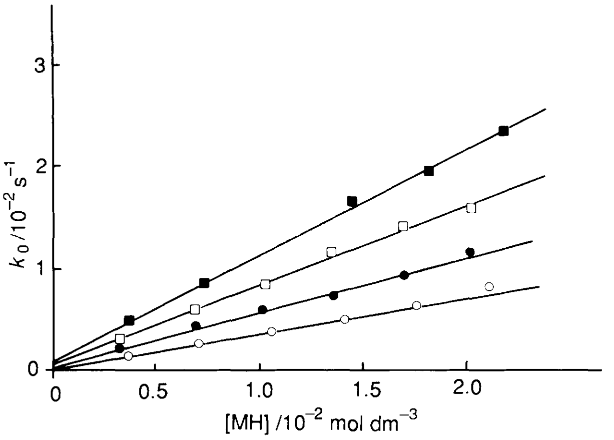


Fig. 2 Dependence of k_0 upon [MH] at different acidities; ○, $[H^+] = 0.78$ mol dm^{-3}; ●, $[H^+] = 1.56$ mol dm^{-3}; □, $[H^+] = 2.35$ mol dm^{-3}; ■, $[H^+] = 3.13$ mol dm^{-3}

Catalysis by SCN^- and $SC(NH_2)_2$ is also marked, but here there are some differences from the halide ion catalysed reactions, in that plots of k_0 *vs.* $[SCN^-]$ although initially linear tend to curve downwards at higher $[SCN^-]$, and there is also some degree of acid catalysis for both SCN^- and $SC(NH_2)_2$ catalysed reactions even at low acidity. The curvature in the SCN^- catalysed reactions may result from a reversibility of the attack by NCSNO, which is well-known in other nitrosation reactions and which is more likely with the more powerful nucleophile. Some of the representative results are given in Table 3. It is reasonable to assume for these catalysed reactions that the limiting value of k_0 at zero $[H^+]$ represents reaction *via* the carbanion, whereas acid catalysis results from reaction with a neutral (rather than negatively charged) form of the substrate. The obvious possibility is the enol form of MH for which K_E is known. This aspect will be discussed more fully later in the paper, when reactions at higher acidity are considered.

From the intercepts of k_0 *vs.* $[H^+]$ for the SCN^- and $SC(NH_2)_2$ catalysed reactions we can deduce the k_2 values [eqn. (3)] for XNO reaction with M^- as 1.1×10^8 and 8.4×10^5 dm^3 mol^{-1} s^{-1} respectively for reactions of ONSCN and $ON\overset{+}{S}C(NH_2)_2$. We thus confirm the now well-established reactivity trend[16] for very reactive substrates of widely differing structure *viz* ClNO *ca.* BrNO > NCSNO > $(NH_2)_2C\overset{+}{S}NO$. One other carbanion reaction has been examined in this way, that derived from malononitrile,[12] which appears to be more reactive than that derived from MH, since reactions of all the XNO species proceed at the encounter limit.

(ii) *Reactions at higher acidity* (> ca. 0.1 mol dm^{-3}). At $[H^+]$ greater than *ca.* 0.1 mol dm^{-3}, all reactions showed acid catalysis. Data for the reactions without added nucleophile catalysts are given in Table 4. The dependence upon [MH] of four different acid concentrations is shown in Fig. 2. These results strongly suggest that under these conditions reaction *via* the carbanion is suppressed and nitrosation occurs by rate-limiting reaction of the enol form of Meldrum's Acid. The small positive intercepts in Fig. 2 again show that the reaction is reversible to a small extent, with an equilibrium constant of about 1000 dm^3 mol^{-1}. It is difficult to get a more precise value because of the error in the measurement of the small intercepts, but the equilibrium constant is sufficiently large to allow the reverse reaction to be ignored in subsequent calculations. The outline is given in Scheme 4 for the reaction of $H_2NO_2^+$ (or NO^+). The third order rate constant [defined by eqn. (4)] has

$$MH \rightleftharpoons \text{Enol } (K_E)$$

$$HNO_2 + H^+ \rightleftharpoons H_2NO_2^+ \text{ (or } NO^+ + H_2O) \; (K_{NO^+})$$

$$H_2NO_2^+ \text{ (or } NO^+) + \text{Enol} \longrightarrow \text{Oxime}$$

Scheme 4

$$\text{Rate} = k_3[\text{Enol}][HNO_2][H^+] \qquad (4)$$

been calculated (*a*) from the $[H^+]$ dependence, and (*b*) from the [MH] dependence, and the published value of K_E. We obtain values of 96 and 88 dm^6 mol^{-2} s^{-1} respectively for k_3 by these two methods. Comparison of these values with k_3 for the carbanion reaction shows that the carbanion is more reactive than the enol by a factor of $> 10^2$. Even so, at the higher acidities the major reaction pathway is *via* the enol since the carbanion concentration is very much reduced under these conditions.

The nucleophile (X^-) catalysed reactions all show the same features. All are acid catalysed (with a very small intercept at $[H^+] = 0$ representing the carbanion reaction) and display the familiar catalytic sequence $Cl^- < Br^- < SCN^- < (NH_2)_2CS$. Analysis of the kinetic data yields the values given in Table 5 for the second order rate constants k_2 for the reaction of the enol with XNO. Table 5 also shows the corresponding values for the carbanion reaction for comparison. Two trends are clear: (*a*) for both substrates the reactivity order of XNO is as expected,[16] and (*b*) that the carbanion is the more reactive intermediate throughout.

Preliminary kinetic experiments with the bromination of MH in water with $[H^+]$ in the range 0.1–1.0 mol dm^{-3} have shown that the observed rate constants are proportional to $[H^+]^{-1}$, which is consistent with reaction *via* the carbanion form. Further experiments are underway at higher acidities to

Table 6 Second order rate constants ($dm^3\ mol^{-1}\ s^{-1}$) for reaction with XNO

XNO	$CH_3C(OH)$=$CHCO_2C_2H_5$	$CH_3C(OH)$=$CHCOCH_3$[a]
ClNO	3.5×10^5	1.0×10^5
BrNO	7.1×10^4	1.4×10^4
NCSNO	1.3×10^3	5.0×10^2

[a] Taken from ref. 9.

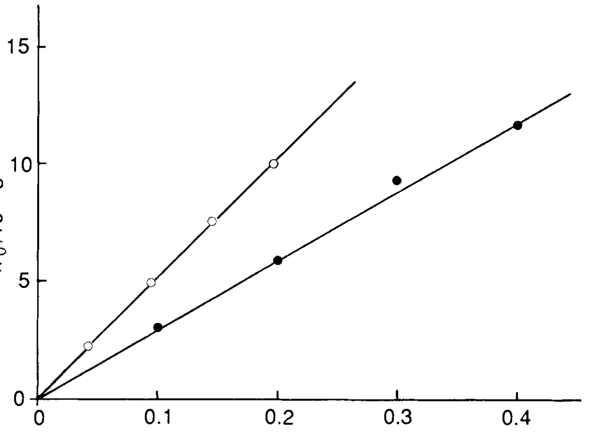


Fig. 3 [EAA] and [H^+] dependence for the nitrosation of EAA; ○, [H^+]; ●, [EAA]

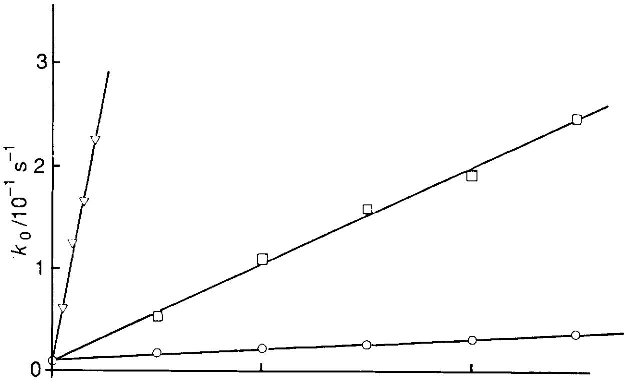
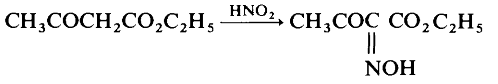


Fig. 4 Nucleophile (X^-) catalysis in the nitrosation of EAA; ○ = Cl^-; □ = Br^-; △ = SCN^-

establish whether reaction *via* the enol form of MH is a general feature of electrophilic addition at high acidities.

Ethyl Acetoacetate (EAA).—For the purposes of comparisons with the results for MH we have examined the nitrosation of ethyl acetoacetate (pK_a 10.7[17]) as an example of a less acidic carbon acid. This substrate has been much studied in terms of its keto $\rightleftharpoons$ enol tautomerism and K_E has been measured[18] as 5.02×10^{-3} in water. Victor Meyer first characterised the product of nitrosation of EAA as ethyl α-oximinoacetate[19] (Scheme 5), which has been isolated from the reaction of EAA with a range of nitrosating agents.



$$CH_3COCH_2CO_2C_2H_5 \xrightarrow{HNO_2} CH_3CO\underset{\underset{NOH}{\|}}{C}\ CO_2C_2H_5$$

Scheme 5

For solubility reasons we were obliged to work in a 20% dioxane–water solvent, and have thus made the assumptions that both pK_a and K_E values of EAA are not significantly altered from the quoted values in water. Attempts to measure K_E in this solvent by NMR spectroscopy were unsuccessful because of the very low enol content. Reaction was found to be first order in [EAA], [HNO_2] and [H^+] and there was no indication of any reversibility of the reaction. Thus the results are consistent with reaction exclusively *via* the enol form. Values of k_3 [eqn. (5), for

$$\text{Rate} = k_3[\text{Enol}][HNO_2][H^+] \qquad (5)$$

reaction with the enol] of 38 and 41 $dm^6\ mol^{-3}\ s^{-1}$ were obtained (see Fig. 3) from the variation of the observed rate constant with (*a*) [H^+], at a constant large excess of EAA and (*b*) [EAA], at a constant [H^+]. These values are roughly comparable with those obtained earlier for the reaction of the enol form of Meldrum's Acid and also for the reaction of the enol form of acetylacetone (pentane-2,4-dione) (36 $dm^6\ mol^{-2}\ s^{-1}$).[9] As expected, nucleophilic catalysis is observed. Fig. 4 shows the results of catalysis of the reaction by Cl^-, Br^- and SCN^-. All of these reactions are also acid-catalysed and, since there is no measurable intercept for the plot of observed rate constant *vs.* [H^+], there is no evidence for a component of the reaction proceeding *via* the carbanion. The derived second order rate constants [k_2 from eqn. (3)] for XNO attack are given in Table 6, where they are compared with the corresponding reactions of the enol of acetylacetone taken from ref. 9. The values are broadly similar as expected given the close structural resemblance of the two enols. Even the most reactive reagent (ClNO) reacts with a rate constant $> 10^4$ less than the encounter limit. The electron-withdrawing influence of the $COCH_3$ and $CO_2C_2H_5$ groups thus has a pronounced deactivating effect on the reactivity of the enol.

Conclusion

Nitrosation (in common with other electrophilic reactions) of carbonyl compounds generally occurs by rate-limiting attack of the reagent XNO at the enol form of the substrate. Under certain experimental conditions the enolisation becomes rate-limiting. If the substrate is sufficiently acidic as a carbon acid then an alternative pathway *via* the carbanion can be identified. This has been achieved in the present work with Meldrum's Acid (pK_a 4.83) at low acidities and previously with trifluoroacetylacetone[20] (pK_a 6.7) and with dimedone[21] (pK_a of the enol 5.2). However the concentration of carbanions derived from ethyl acetoacetate (pK_a 10.7) and acetylacetone[9] (pK_a 8.87) are not sufficient under our range of acidity to provide a significant reaction pathway *via* a carbanion intermediate. However, the carbanion derived from malononitrile (pK_a 11.4) is so reactive that it reacts with all of the reagents discussed in the present work at the encounter limit, resulting in a reaction pathway *via* the carbanion even in the pH range 2–4.

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