# Electrophilic Substitution in Malonamide. Evidence for Reaction *via* the Enol Tautomer

**D. Lyn H. Williams* and Ling Xia**
*Chemistry Department, University Science Laboratories, South Road, Durham, UK DH1 3LE*

The kinetics of the nitrosation, bromination and iodination of malonamide [MA] have been studied in water at 25 °C. Throughout, reaction was first order in [MA]. At low acidity and relatively high [$I_2$], reactions were fully zero-order in [$I_2$] and acid-catalysed. At higher acidity and lower [$I_2$] reaction was first-order in [$I_2$] and not now acid-catalysed. Similar first-order behaviour was found for bromination and nitrosation (by BrNO and ONSCN generated *in situ*). It was not possible by changing the reaction conditions to achieve the zero-order pattern with either bromination or nitrosation. The results are consistent with a mechanism involving reaction of the electrophile with an intermediate derived from MA which we suggest is the enol tautomer. For iodination either enolisation or reaction of the enol can be made rate-limiting. For enolisation the value of the rate constant $k_e$ (in Rate = $k_e$[MA][$H^+$]) was found to be $3.3 \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$. The results also suggest that $I_2$, $Br_2$, BrNO and ONSCN react with the enol at or close to the encounter controlled limit, enabling a value for $K_E$ (the equilibrium constant for enolisation) of $(4 \pm 2) \times 10^{-10}$ to be obtained. The methylene protons in MA are readily exchanged with D from the solvent in an acid catalysed process. The enolisation of $CD_2(COND_2)_2$ is slower than that of $CH_2(CONH_2)_2$ by a factor of 2.3 and the deuterium solvent isotope effect is close to 1. The mechanism of enolisation of MA is discussed.

A number of 2-halo derivatives of malonamide (MA) have been prepared using different brominating[1] and iodinating[2] agents; sometimes the reaction goes further to give the dihalo derivatives. Similarly the oxime [eqn. (1)] has been prepared by a

$$CH_2(CONH_2)_2 + HNO_2 \xrightarrow{H^+} HON{=}C(CONH_2)_2 + H_2O \quad (1)$$

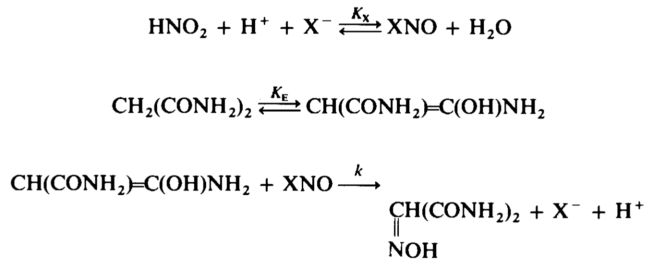
*C*-nitrosation reaction. No mechanistic studies of these reactions appear to have been carried out. It seems possible that such reactions proceed *via* an enol intermediate, although enol intermediates from amides do not appear to have been described in the literature. Currently there is much renewed interest in the chemistry of enols,[4] one aspect of which centres around the possibility of enol tautomers of carbonyl-containing compounds other than ketones, notably carboxylic acids and esters. This work presents an opportunity to examine the possibility that enol tautomers of an amide exist as reactive intermediates.

O'Neill and Hegarty[5] have synthesised and characterised enols derived from a carboxylic acid and an ester, using the Fuson method (developed for ketones) based on the destabilisation of the keto form (relative to the enol) by the use of very large substituent groups, $C_6Me_5$ in this case. There are a number of references[6] in which enol forms of malonic and methylmalonic acids have been detected kinetically using scavenging halogenation reactions and finding a rate law zero-order in [halogen]. This is an extension of the classical work of Lapworth[7] who did the pioneering work with simple ketones. We wished to establish whether similar reaction pathways could be identified for the corresponding reactions of amides and chose to undertake the kinetics of the reactions of malonamide given the earlier observations[1,2,3] that the substitution products could readily be synthesised. A preliminary account of this work has already been published.[8]

## Results

*Nitrosation.*—Reaction occurred readily between MA and nitrous acid in acid solution, but unfortunately at a rate which allowed the spontaneous decomposition of nitrous acid to intervene and so make a quantitative kinetic study more difficult. To overcome this problem we examined the nucleophile catalysed reactions using $Br^-$ and $SCN^-$ as catalysts when the actual nitrosating species are known to be BrNO and ONSCN respectively, generated in solution. The catalytic effect of $Cl^-$ was not sufficient to allow the rate of decomposition of $HNO_2$ to be neglected. Reactions were followed spectrophotometrically, noting the disappearance of $HNO_2$ at 370 nm. All kinetic experiments were carried out with $[MA]_0 \gg [HNO_2]_0$ and excellent first-order behaviour was obtained throughout. Reaction was also first-order in [MA] and acid catalysed. The results are given in Tables 1 and 2. The plot of the measured first order rate constant $k_1$ (defined by $-d[HNO_2]/dt = k_1[HNO_2]$) *vs.* [MA] is an excellent straight line which passes through the origin. However, the plot of $k_1$ *vs.* [$H^+$] shows a distinct upward curvature. This was shown not to be an ionic strength effect and has previously been noted[9] for example in the nitrosation of $HN_3$ and $NH_2NH_3$, and is probably due to activity effects on the equilibria involved in the generation of the free nitrosating agent. Catalysis by both $Br^-$ and $SCN^-$ occurs in the expected fashion and the results are shown in Table 3. For both catalysts there is a linear dependence of $k_1$ upon [$Br^-$] or [$SCN^-$], with a small positive intercept in both cases, which represents the contribution due to the uncatalysed reaction.

If we assume that reaction occurs *via* the enol form of MA as set out in Scheme 1, then it is easy to obtain values of $kK_E$: (*a*) for



$$HNO_2 + H^+ + X^- \overset{K_X}{\rightleftharpoons} XNO + H_2O$$

$$CH_2(CONH_2)_2 \overset{K_E}{\rightleftharpoons} CH(CONH_2){=}C(OH)NH_2$$

$$CH(CONH_2){=}C(OH)NH_2 + XNO \xrightarrow{k} \underset{\substack{\| \\ NOH}}{C}H(CONH_2)_2 + X^- + H^+$$

Scheme 1

**Table 1** First-order rate constants ($k_1$) for the reaction of MA with $HNO_2$ ($7.1 \times 10^{-3}$ mol dm$^{-3}$) containing $H^+$ ($7.2 \times 10^{-2}$ mol dm$^{-3}$) and $Br^-$ (0.598 mol dm$^{-3}$)

| [MA]/mol dm$^{-3}$ | $k_1/10^{-3}$ s$^{-1}$ |
|---|---|
| 0.072 | 0.50 |
| 0.108 | 0.74 |
| 0.162 | 1.16 |
| 0.216 | 1.52 |
| 0.252 | 1.90 |
| 0.288 | 2.20 |
| 0.324 | 2.50 |
| 0.361 | 2.79 |
| 0.405 | 3.12 |

**Table 2** First-order rate constants $k_1$ for the reaction of MA (0.201 mol dm$^{-3}$) with $HNO_2$ ($1.0 \times 10^{-2}$ mol dm$^{-3}$) containing $Br^-$ (0.600 mol dm$^{-3}$) and constant ionic strength (1.20 mol dm$^{-3}$ made up with $NaClO_4$)

| [$H^+$]/mol dm$^{-3}$ | $k_1/10^{-2}$ s$^{-1}$ |
|---|---|
| 0.10 | 0.32 |
| 0.20 | 0.83 |
| 0.25 | 1.14 |
| 0.30 | 1.47 |
| 0.35 | 1.94 |
| 0.40 | 2.26 |
| 0.50 | 3.06 |

**Table 3** First-order rate constants ($k_1$) for the nitrosation of MA catalysed by $Br^-$ or $SCN^-$ with $HNO_2$ ($7.2 \times 10^{-3}$ mol dm$^{-3}$) and $H^+$ ($7 \times 10^{-2}$ mol dm$^{-3}$)

| [MA]/mol dm$^{-3}$ | [$Br^-$]/mol dm$^{-3}$ | [$SCN^-$]/mol dm$^{-3}$ | $k_1/10^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 0.203 | 0.14 | — | 0.41 |
| 0.203 | 0.21 | — | 0.59 |
| 0.203 | 0.28 | — | 0.73 |
| 0.203 | 0.35 | — | 0.90 |
| 0.203 | 0.42 | — | 1.05 |
| 0.203 | 0.49 | — | 1.21 |
| 0.203 | 0.56 | — | 1.38 |
| 0.200 | — | 0.0020 | 1.45 |
| 0.200 | — | 0.0040 | 2.39 |
| 0.200 | — | 0.0060 | 3.61 |
| 0.200 | — | 0.0080 | 4.42 |
| 0.200 | — | 0.0100 | 5.33 |

the BrNO reaction of 3.6 dm$^3$ mol$^{-1}$ s$^{-1}$ (from the data in Table 1) and 3.1 dm$^3$ mol$^{-1}$ s$^{-1}$ (from the data in Table 3); (*b*) for the ONSCN reaction of 1.2 dm$^3$ mol$^{-1}$ s$^{-1}$ (from the data in Table 3).

There was some evidence of a change towards a zero-order dependence on [$HNO_2$] at very high [$Br^-$] and [$SCN^-$] but in neither case was it possible to obtain a reliable value for the zero-order rate constant. At high [$SCN^-$] particularly there are difficulties which arise from the substantial concentrations of ONSCN which are formed and ONSCN decomposition then becomes a major factor.

*Iodination.*—These experiments were carried out with $[MA]_0 \gg [I_2]_0$ by monitoring the disappearance of the iodine absorbance at 460 nm. With $[I_2] \sim 6 \times 10^{-4}$ mol dm$^{-3}$ and acid present in the range of 0.01–0.10 mol dm$^{-3}$ ($HClO_4$) reactions were perfectly zero-order in [$I_2$] as shown by the linearity of the absorbance–time plots up to 90% reaction. Reactions were first-order in [MA] and acid-catalysed as shown by the results given in Table 4. Zero order rate constants ($k_0$) were obtained from the slopes of the absorbance–time plots and the extinction coefficient of $I_2$ at 460 nm (697 dm$^3$ mol$^{-1}$ cm$^{-1}$). The plot of $k_0$ *vs.* [MA] is perfectly linear and passes through the origin, whereas the plot of $k_0$ *vs.* [$H^+$] whilst also yielding an excellent line, has a small positive intercept at [$H^+$] = 0. These data establish the rate equation given in eqn. (2) yielding

$$\text{Rate} = k_0 = k_e'[\text{MA}] + k_e[\text{MA}][\text{H}^+] \qquad (2)$$

values of $k_e'$ $2.5 \times 10^{-5}$ s$^{-1}$ and $k_e$ $3.3 \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$ from the plot of $k_0$ *vs.* [$H^+$]. These values produced a calculated value for the slope of the plot of $k_0$ *vs.* [MA] of $1.9 \times 10^{-4}$ s$^{-1}$ compared with the experimental value of $2.1 \times 10^{-4}$ s$^{-1}$, which is an acceptable degree of agreement.

Clearly under these conditions we are measuring the rate of formation of an intermediate (probably the enol) by an acid-catalysed pathway together with a small component *via* an uncatalysed pathway. The pattern is the same as that which is well-established in the enolisation of simple ketones in acid solution. Under these conditions the limiting situation $k_k[H^+] \ll k[I_2]$ (from Scheme 2) applies. However at lower [$I_2$] and higher [$H^+$] we are able to achieve the other limiting condition $k_k[H^+] \gg k[I_2]$ when the rate of ketonisation of the enol now is much larger than the rate of reaction of the enol with iodine. This predicts a change to first-order kinetics, which is found experimentally. Details are given in Table 5. This limiting form can also be achieved by the addition of $I^-$ which reduces the [$I_2$] generating the less reactive iodinating species $I_3^-$. Reaction is, as expected, again first-order in [MA] but is now independent of the acidity. This excludes a pathway *via* the enolate ion. The $kK_E$ product obtained from the results in Table 5 has a value 4.6 dm$^3$ mol$^{-1}$ s$^{-1}$.

$$\text{MA} \xrightleftharpoons[k_k,[\text{H}^+]]{k_e,[\text{H}^+]} \text{Enol}$$

$$\text{Enol} + \text{I}_2 \xrightarrow{k} \text{Product}$$

**Scheme 2**

*Bromination.*—Unless the ratio of reactants [MA]/[$Br_2$] was greater than *ca.* 27, unusual absorbance–time plots were obtained which could be interpreted qualitatively by the incursion of dibromide formation. This was not a problem with iodination, possibly because of a steric problem with the larger iodine molecule. However, with [MA] = 0.100 mol dm$^{-3}$ and [$Br_2$] = $3.7 \times 10^{-3}$ mol dm$^{-3}$, reactions were perfectly first-order in [$Br_2$] and the first-order rate constants were independent of acidity in the range 0.01–0.10 mol dm$^{-3}$ $HClO_4$ as shown in Table 6, yielding a value of $kK_E$ of 1.5 dm$^3$ mol$^{-1}$ s$^{-1}$. It was not possible to change fully to the zero-order kinetics situation encountered in iodination because of the dibromination problem.

*Kinetic Isotope Effects.*—Deuteriated malonamide (DMA) was prepared by isotopic exchange with $D_2O$, and rate measurements were carried out for iodination under zero-order conditions *i.e.* when enolisation is rate limiting (at $[I_2] \sim 6 \times 10^{-4}$ mol dm$^{-3}$ and $[H^+] \sim 0.01$ mol dm$^{-3}$). Rate constants were obtained at four different substrate concentrations for the reactions of MA in $H_2SO_4/H_2O$ and in $D_2SO_4/D_2O$ and for DMA in $H_2SO_4/H_2O$ and in $D_2SO_4/D_2O$. The results are given in Table 7 and yield values of the substrate kinetic isotope effect

**Table 4** Zero-order rate constants ($k_0$) for the iodination of MA at [$I_2$] 6.5 × $10^{-4}$ mol $dm^{-3}$

| [MA]/mol $dm^{-3}$ | [$H^+$]/mol $dm^{-3}$ | $k_0/10^{-6}$ mol $dm^{-3}$ $s^{-1}$ |
|---|---|---|
| 0.0197 | 0.01 | 1.11 |
| 0.0197 | 0.02 | 1.84 |
| 0.0197 | 0.03 | 2.44 |
| 0.0197 | 0.04 | 3.06 |
| 0.0197 | 0.05 | 3.89 |
| 0.0197 | 0.06 | 4.45 |
| 0.0197 | 0.07 | 5.01 |
| 0.0197 | 0.08 | 5.83 |
| 0.0197 | 0.09 | 6.34 |
| 0.0197 | 0.10 | 7.01 |
| 0.0147 | 0.05 | 3.35 |
| 0.0246 | 0.05 | 5.41 |
| 0.0369 | 0.05 | 7.89 |
| 0.0491 | 0.05 | 10.5 |
| 0.0590 | 0.05 | 12.8 |
| 0.0737 | 0.05 | 15.7 |

**Table 5** First-order rate constants ($k_1$) for the iodination of MA at [$I_2$] 2.1 × $10^{-4}$ mol $dm^{-3}$

| [$H^+$]/mol $dm^{-3}$ | [MA]/$10^{-3}$ mol $dm^{-3}$ | $k_1/10^{-2}$ $s^{-1}$ |
|---|---|---|
| 0.300 | 5.21 | 1.75 |
| 0.375 | 5.21 | 2.23 |
| 0.437 | 5.21 | 2.50 |
| 0.500 | 5.21 | 2.50 |
| 0.550 | 5.21 | 2.50 |
| 0.450 | 4.04 | 1.88 |
| 0.450 | 6.05 | 2.81 |
| 0.450 | 8.07 | 3.76 |
| 0.450 | 10.1 | 4.57 |
| 0.450 | 11.6 | 5.38 |

**Table 6** First-order rate constants ($k_1$) for the bromination of MA (0.100 mol $dm^{-3}$) with [$Br_2$] 3.7 × $10^{-3}$ mol $dm^{-3}$

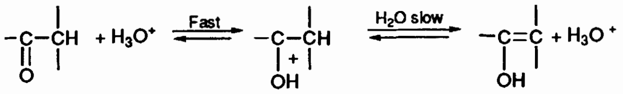
| [$H^+$]/mol $dm^{-3}$ | $k_1/s^{-1}$ |
|---|---|
| 0.01 | 0.134 |
| 0.02 | 0.147 |
| 0.03 | 0.135 |
| 0.04 | 0.142 |
| 0.05 | 0.146 |
| 0.06 | 0.144 |
| 0.07 | 0.147 |
| 0.08 | 0.143 |
| 0.09 | 0.150 |
| 0.10 | 0.149 |
| 0.15 | 0.180 |
| 0.20 | 0.202 |
| 0.40 | 0.275 |

$(k_e)_H/(k_e)_D$ of 2.30 and 2.20 and values of the solvent isotope effect $(k_e)H_2O/(k_e)D_2O$ of 1.09 and 1.05.

A few experiments were carried out using proton NMR noting the disappearance of the resonance at $\delta$ 5.7 due to the methylene protons. In the absence of added mineral acid the change was slow and was 80% complete in one day and 98% complete after seven days. In the presence of $D_2SO_4$ (*ca.* 0.5 mol $dm^{-3}$) the exchange was very much quicker being 84% complete in 5 min and 96% complete in 42 min.

## Discussion

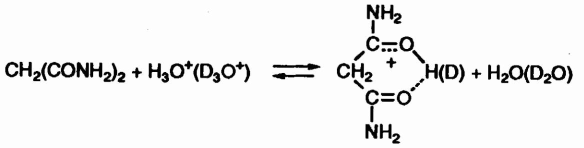
The kinetic results of iodination of MA at relatively high [$I_2$] and low [$H^+$] show clearly that we are measuring the rate of formation of an intermediate from MA by an acid-catalysed (with a small component of an uncatalysed) process. The value of $k_e$ [eqn. (2)] is significantly larger than is the corresponding value for a simple ketone such as acetone[10] ($\sim 2.8 \times 10^{-5}$ $dm^3$ $mol^{-1}$ $s^{-1}$) derived from halogenation and nitrosation scavenging reactions, and also from hydrogen-isotope exchange reactions. The most likely explanation for this is that the methylene protons in MA are significantly more acidic than are the protons in acetone, as a consequence of the electron-withdrawing power of the $CONH_2$ group. For many simple ketones $k_e$ for the acid-catalysed process is not very sensitive to structure no doubt[11] due to the opposing effects of say electron withdrawal on the extent of *O*-protonation and on the rate of proton removal (see Scheme 3), but larger values have been reported for the more acidic carbonyl compounds such as indan-2-one.[12] Clearly in our case the effect on the proton acidity could be much the larger effect. Alternatively the high reactivity of MA may derive from the added stabilisation given to the *O*-protonated intermediate by intramolecular hydrogen-bonding [see eqn. (3) later]. It was not possible with our nitrosation experiments to achieve the limiting case when the nitrosation rate is much larger than the ketonisation rate and with bromination there appeared to be problems arising from di-bromination.



**Scheme 3**

Using iodine as the scavenger we found that enolisation of MA is subject to a kinetic isotope effect of 2.2–2.3 when the methylene protons were exchanged for deuterium. This is significantly smaller than the value found for acetone enolisation[13] ($k_H/k_D$ 6.7) and a number of other similar reactions, but we consider it still to be a primary kinetic isotope effect. The corresponding value for acetylacetone (which is a closer model for MA) is 4.5.[14] Maximum isotope effects in proton transfer reactions tend to occur when $\Delta pK$ is 0, and will be smaller for both 'early' and 'late' transition states. The greater expected acidity of the protons in MA and acetylacetone (when compared with acetone) should be examples of the latter.

The generally accepted mechanism for the much studied acid-catalysed enolisation of ketones is the two-stage process (given in Scheme 3) first proposed by Pedersen.[15] Our results for MA are consistent with this. This mechanism does predict a kinetic solvent isotope effect $k_{H_2O}/k_{D_2O} < 1$ for the enolisation rate constant and a number of such values have been reported[13,16] usually around 0.5, resulting from the greater extent of *O*-protonation in the deuteriated solvent. However, we find from the results in Table 7 values very close to unity *i.e.* 1.09 and 1.05 for the enolisation of MA in $H_2SO_4$–$H_2O$/$D_2SO_4$–$D_2O$ and for DMA in $H_2SO_4$–$H_2O$/$D_2SO_4$–$D_2O$. It is not immediately apparent why this is so, but a possible explanation is that the 'normal' (*i.e.* ~ 0.5) is offset by another isotope effect on *O*-protonation, if the intermediate hydroxycarbocation is involved in intramolecular hydrogen-bonding as outlined in eqn. (3).



(3)

When reactions are first-order in the electrophile concentration, it is clear that now the reaction of the enol is rate-limiting. We have been able to obtain for each of the electrophiles ($I_2$,

**Table 7** Values of zero-order rate constants ($k_0$) for the iodination of MA and DMA in $H_2SO_4$–$H_2O$ and $D_2SO_4$–$D_2O$ (total [$H^+$] or [$D^+$] 0.0100 mol dm$^{-3}$) with $I_2$ ($6 \times 10^{-4}$ mol dm$^{-3}$)

| [MA]/mol dm$^{-3}$ | [DMA]/mol dm$^{-3}$ | $k_0/10^{-6}$ mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|
| $H_2SO_4$–$H_2O$ | | |
| 0.0175 | — | 1.28 |
| 0.0264 | — | 2.00 |
| 0.0398 | — | 2.97 |
| 0.0530 | — | 3.79 |
| — | 0.0165 | 0.54 |
| — | 0.0290 | 0.95 |
| | 0.0411 | 1.34 |
| | 0.0513 | 1.60 |
| $D_2SO_4$–$D_2O$ | | |
| 0.0167 | — | 1.14 |
| 0.0277 | — | 1.80 |
| 0.0399 | — | 2.52 |
| 0.0539 | — | 3.49 |
| — | 0.0145 | 0.40 |
| — | 0.0260 | 0.68 |
| — | 0.0384 | 1.04 |
| — | 0.0488 | 1.36 |

**Table 8** Values of $kK_E$ for different electrophiles

| Electrophile | $kK_E$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|
| BrNO | 3.3 |
| ONSCN | 1.2 |
| $I_2$ | 4.6 |
| $Br_2$ | 1.5 |

$Br_2$, BrNO, ONSCN) values of $kK_E$ (from Scheme 1), *i.e.* the product of the rate constant for reaction of the enol and the equilibrium constant for enol formation. These values are collected in Table 8, and are remarkably constant given the wide range of reactivity usually associated with this group of electrophiles. The only sensible explanation is that the reactions with the enol are all at or near to the diffusion controlled limit. This is not unreasonable, since the enol from MA is expected to be a very reactive species towards electrophilic reagents. If we accept the value of $7 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ for the diffusion controlled bimolecular rate constant for reaction in water at 25 °C then a value for $K_E$ emerges as $(4 \pm 2) \times 10^{-10}$. This is essentially the approach adopted by Toullec[17] for $K_E$ determinations for simple ketones using very low halogen concentrations to ensure a first-order kinetic dependence upon [halogen]. Our value for MA compares with the now accepted value of $6.0 \times 10^{-9}$ for acetone[18] and recent estimated values[19] for malonic and methylmalonic acids of *ca.* $1 \times 10^{-8}$.

Finally we report that it is possible to measure the rate of methylene proton exchange in MA with the solvent by proton NMR using $D_2SO_4/D_2O$. We obtained no quantitative data (though it would be perfectly possible to do so) but it was quite clear that the process, as expected is acid-catalysed. Detailed measurements have been reported recently[20] of the corresponding exchange reaction in malonic acid.

## Experimental

*Materials.*—Malonamide was purified by recrystallisation from water and dried (m.p. 169–171 °C, lit.[1] 170 °C). All other chemicals were of the highest possible purity available. Stock solutions of sodium nitrite were made up daily as required. Iodine solutions were prepared by saturation in distilled water and concentrations obtained by thiosulfate titration. Bromine solutions were also made up in distilled water and concentrations determined by thiosulfate titration and also from the absorbance at 393 nm ($\varepsilon$ 128 dm$^3$ mol$^{-1}$ cm$^{-1}$). Deuterium labelled malonamide (DMA) was prepared by dissolving MA in $D_2O$ and monitored by $^1H$ NMR. After one week the resonance at $\delta$ 5.7 disappeared completely and the solution was evaporated and the solid dried.

*Kinetics.*—Iodination and nitrosation experiments were carried out using a conventional UV spectrophotometer interfaced with a PC. Nitrosation was followed by the disappearance of the absorbance at 370 nm and iodination similarly at 460 nm. For the more rapid bromination reactions (using a higher [MA]) measurements were made by stopped-flow spectrophotometry noting the disappearance of bromine at 393 nm. First-order rate constants were obtained using a measured infinity value and a standard program; zero-order rate constants were obtained from the slope of the absorbance time plots and the extinction coefficient of the absorbing species. The rate constants quoted are the mean values of at least four separate determinations and the reproducibility was always better than ±4%.

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