

Evidence for the Enol form of Malonamide

D. Lyn H. Williams* and Ling Xia

Chemistry Department, University Science Laboratories, South Road, Durham DH1 3LE, UK

At low acid concentration the reaction of iodine with malonamide in water is zero order in $[I_2]$, consistent with a rate-limiting enolisation.

Recently there has been much interest in the chemistry of enols, particularly those derived from carbonyl-group containing compounds other than ketones, including carboxylic acids and esters.¹⁻³ In principle, amides should be capable of enolisation and subsequent electrophilic addition, but there is (as far as we are aware) no evidence in the literature which suggests that this is so. One report⁴ claims (on the basis of IR evidence) that dicyanoacetamide **1** exists largely or completely in the enol form in the solid state. Electrophilic substitution (halogenation⁵ and nitrosation⁶) at the α -carbon atom in malonamide **2** is known as a preparative reaction, but no kinetic or other studies seem to have been performed to establish the nature of any intermediates and other features of the reaction mechanisms.

We now report the kinetic results of the reaction of iodine with malonamide in dilute aqueous solution at 25 °C. Reaction was followed spectrophotometrically at 459 nm noting the disappearance of the iodine absorbance. All experiments were

carried out with a large excess of malonamide over iodine; typical concentrations used were, malonamide $1.5\text{--}7.0 \times 10^{-2}$ mol dm⁻³, iodine 6.5×10^{-4} mol dm⁻³ and perchloric acid 0.01–0.10 mol dm⁻³. Under these conditions the absorbance–time plots were linear, indicating a zero-order dependence upon $[I_2]$. The data in Table 1 (which gives the zero-order rate constants k_0 as a function of [malonamide] and $[H^+]$) enable

$$\text{Rate} = k' [\text{MA}] + k'' [\text{H}^+][\text{MA}] = k_0 \quad (1)$$

the rate equation (1) to be established. Values of k' and k'' are respectively 2.5×10^{-5} s⁻¹ and 3.3×10^{-3} dm³ mol⁻¹ s⁻¹. Clearly we are measuring the formation of an intermediate which then reacts rapidly with iodine. The most likely

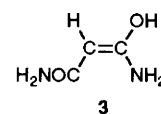
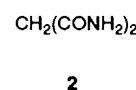
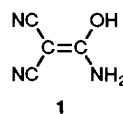
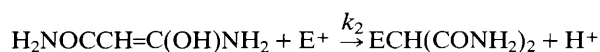


Table 1 Zero-order rate constants k_0 for the reaction of iodine (6×10^{-4} mol dm $^{-3}$) with malonamide (MA)

$10^2[\text{MA}]/\text{mol dm}^{-3}$	$[\text{H}^+]/\text{mol dm}^{-3}$	$10^6k_0/\text{mol dm}^{-3}\text{s}^{-1}$
1.47	0.051	3.35
2.46	0.051	5.41
3.69	0.051	7.89
4.91	0.051	10.5
5.90	0.051	12.8
7.37	0.051	15.7
1.97	0.010	1.11
1.97	0.020	1.84
1.97	0.030	2.44
1.97	0.040	3.06
1.97	0.050	3.89
1.97	0.060	4.45
1.97	0.070	5.01
1.97	0.080	5.83
1.97	0.090	6.34
1.97	0.100	7.01

explanation is that we are looking at an acid-catalysed enolisation to form **3**, together with a small component of a non-acid catalysed pathway. This is commonly the situation with enolisation of simple ketones. The value of k'' is significantly larger than that measured for simple ketones such as acetone⁷ (3.8×10^{-5} dm 3 mol $^{-1}$ s $^{-1}$), no doubt reflecting the greater acidity of the methylene protons brought about by the second CONH $_2$ group. The enol form of malonic acid had been identified by similar kinetic procedures both with halogenation⁸ and nitrosation³ as the scavenging reactions. For malonic acid, however, acid catalysis is brought about intramolecularly, and so no comparison can be made with the malonamide reaction.

At lower $[\text{I}_2]$ and also with bromine at low concentrations (both at higher acid concentrations than previously) the reaction became first-order in [halogen]. Similarly with nitrous acid in the presence of Br $^-$ or SCN $^-$ (when the effective reagents are BrNO and ONSCN, respectively) reactions were also first order in $[\text{HNO}_2]$. Under these conditions, the reaction of the enol with the electrophile (E $^+$) is rate-limiting (see Scheme 1). Kinetic analysis of all four

**Scheme 1****Table 2** Values of k_2K_E for different electrophiles

Electrophile	$k_2K_E/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$
I $_2$	4.12
Br $_2$	1.45
BrNO	3.92
ONSCN	1.17

reactions yields values of k_2K_E given in Table 2. These values are reasonably constant considering the wide range of reactions involved, and imply that all of the reagents react with the enol at the encounter limit. This is not an unreasonable suggestion as **3** would be predicted to be a very reactive species. If we assume the limiting value for k_2 to be *ca.* 7×10^9 dm 3 mol $^{-1}$ s $^{-1}$ for reactions in water at 25 °C, then we obtain a value for K_E of $4 (\pm 2) \times 10^{-10}$, which compares with the measured value⁹ for acetone of 6.0×10^{-9} .

As expected, and as has been shown for malonic acid,¹⁰ hydrogen atom exchange occurs readily between the solvent and the methylene protons in malonamide. We have examined this in a semi-quantitative way by ^1H NMR spectroscopy noting the disappearance of the signal due to the methylene protons in a deuteriated solvent. The exchange process is clearly acid-catalysed and almost certainly involves enolisation and re-ketonisation as is the case in simple ketones.

Received, 15th April 1992; Com. 2/01983C

References

- P. O'Neill and A. F. Hegarty, *J. Chem. Soc., Chem. Commun.*, 1987, 744.
- Y. Chiang, A. J. Kresge, P. Pruszyński, N. R. Schepp and J. Wirz, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 792.
- A. Graham and D. L. H. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 407.
- S. Trofimenko, E. L. Little and H. F. Mower, *J. Org. Chem.*, 1962, **27**, 433.
- J. V. Backes, R. W. West and M. A. Whitley, *J. Chem. Soc.*, 1921, **119**, 359.
- M. A. Whitley, *J. Chem. Soc.*, 1900, **77**, 1040; 1903, **83**, 24; M. Conrad and A. Schulze, *Berichte*, 1909, **42**, 729.
- J. R. Leis, M. E. Peña, D. L. H. Williams and S. D. Mawson, *J. Chem. Soc., Perkin Trans. 2*, 1988, 157.
- V. M. Bhale, S. L. Bafna and W. V. Bhagwat, *Z. Phys. Chem.*, 1957, **12**, 302; K. R. Leopold and A. Haim, *Int. J. Chem. Kinet.*, 1977, **9**, 83 and earlier references therein.
- Y. Chiang, A. J. Kresge and Y. S. Tang, *J. Am. Chem. Soc.*, 1984, **106**, 460.
- E. W. Hansen and P. Ruoff, *J. Phys. Chem.*, 1988, **92**, 2641.