Kinetics of the Enolisation Reaction of 2-Acetylfuran, 2-Acetyl-*N*-methylpyrrole and 3-Acetyl-*N*-methylpyrrole†

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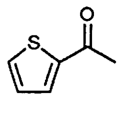
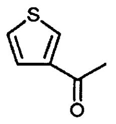
Kinetic results are reported on the rates of enolisation of 2-acetylfuran, 2-acetyl-*N*-methylpyrrole and 3-acetyl-*N*-methylpyrrole in water, in buffer, in dilute hydrochloric acid solutions, in dilute sodium hydroxide solutions and in the presence of several metal ion salts, as measured by their rates of halogenation. The results have been compared with those of corresponding reactions of 2-acetylthiophene, 3-acetylthiophene and acetophenone. In metal ion promoted reactions the catalytic effects observed are probably due to coordination of the carbonyl oxygen in the reaction transition states, while there is no evidence of participation of the heteroatoms of the aromatic rings in chelation. Metal activating factors are particularly high for the acetylpyrroles where, for example, Cu^{2+} is up to 740 times more effective than the proton in catalysing the enolisation reaction of 3-acetyl-*N*-methylpyrrole. This is in agreement with the high negative charge density on the oxygen atom recently observed by NMR spectroscopy for the acetylpyrroles as compared to acetylfurans, acetylthiophenes and acetophenone.

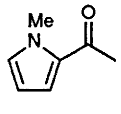
In sharp contrast to acetophenones, relatively little work[1–3] is available in the literature on the enolisation reaction of heteroaromatic ketones. We have recently studied the kinetics of the enolisation of 2- and 3-acetylthiophenes (**2AT** and **3AT**) and compared the results obtained[4] with the corresponding data for acetophenone.[4–6] Acetophenone and the two acetylthiophenes **2AT** and **3AT** display similar reactivities under a variety of experimental conditions. It was also found that particular metal ions (Cd^{2+} and Zn^{2+}) catalyse the 'water' enolisation reaction of these aromatic ketones in a similar fashion, Zn^{2+} being more effective than Cd^{2+}, while Ni^{2+} shows no appreciable effect. The observed rate accelerations were attributed in all cases to the participation of Zn^{2+} or Cd^{2+} in stabilising the corresponding reaction transition states by coordination with the carbonyl oxygen atom. For **2AT** no evidence of participation of the sulfur atom in chelation was found. However the observed metal activating factors (MAF)[7] were far from dramatic, the proton being 20–400 times more effective as a catalyst than either Cd^{2+} or Zn^{2+}. It now seems appropriate to extend these studies[4] to different heterocyclic ketones looking in particular at the role of nitrogen and oxygen as heteroatoms in metal ion catalysed enolisation reactions. Indeed, coordination of the heteroatom with some Lewis acid catalysts is very strong with pyrrole, as observed in particular electrophilic substitution reactions.[8] Furan would similarly coordinate better than thiophene.[9] Furthermore it has been shown by Cox[1] that complex formation between 2-acetylpyridine and Zn^{2+}, Ni^{2+} and Cu^{2+} leads to rates up to 2 × 10^3 times larger than that of uncomplexed substrate, with both nitrogen and oxygen atoms of 2-acetylpyridine involved in coordination in the transition state of the reaction. Therefore we have measured the rate of halogenation (iodination or bromination) of 2-acetyl-*N*-methylpyrrole (**2AP**), 3-acetyl-*N*-methylpyrrole (**3AP**) and 2-acetylfuran (**2AF**) in water, in dilute solutions of hydrochloric acid and of sodium hydroxide, in acetate buffers and in the presence of several metal ion salts at 25 °C. We have also extended previous measurements[4] on **2AT**, **3AT** and acetophenone, where necessary for comparison.



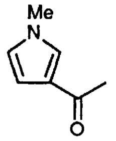
2AT



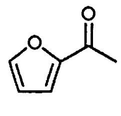
3AT



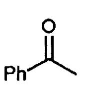
2AP



3AP



2AF



A

The reactions are zero-order with respect to halogen concentration, with the rate-determining step being the formation of the enol or enolate ion. The results are discussed in relation to those of earlier studies on related systems.[4–6]

Experimental

Materials.—**2AP**, **3AP** and **2AF** were commercial samples (Aldrich), purified by distillation under reduced pressure. **2AT**, **3AT** and acetophenone were as previously described.[4]

All inorganic salts [KCl, $NaClO_4$, KI, NaBr, $ZnCl_2$, $CdCl_2$, $NiCl_2$, $Cu(NO_3)_2$] and halogens (I_2 and Br_2) were samples of AnalaR grade (Aldrich, Merck or Carlo Erba) and were used without further purification.

Kinetic Measurements.—The enolisation reactions were followed by monitoring spectrophotometrically the rate of halogenation of the substrate as previously described[4] by using a

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Varian DMS 90 spectrophotometer or a Kontron Uvikon 860 equipped with a hi-tech rapid kinetic accessory in aqueous solutions at 25 ± 0.1 °C and an ionic strength of 0.3 mol dm^{-3} made by the addition of the required amounts of KCl or $NaClO_4$.

For the iodination reactions a zero-order loss of iodine was observed and there was no evidence of reversibility. The rate law had the form shown in eqn. (1) where S refers to the substrate **2AP**, **3AP** or **2AF** and $[I_2]_{tot}$ refers to the total concentration of iodine ($[I_2] + [I_3^-]$).

$$-d[I_2]_{tot}/dt = k_e[S] \qquad (1)$$

Bromination reactions in dilute hydroxide[10] were irreversible and zero-order in OBr^-. The rate law for bromination was similarly given by eqn. (2).

$$-d[OBr^-]/dt = k_e[S] \qquad (2)$$

Results

Iodination of **2AP**, **3AP** *and* **2AF** *in Dilute Hydrochloric Acid.*—Reaction rates were measured with concentration of the substrate in the range 1–3 × 10^{-2} mol dm^{-3} and HCl concentration in the range 2–60 × 10^{-3} mol dm^{-3}. The observed rate law was given by eqn. (3) with k_e being of the form shown in eqn. (1).

$$k_e = k_0 + k_H[H^+] \qquad (3)$$

The following results were obtained:

2AP: $k_0 = 5.4\,(\pm 0.6) \pm 10^{-8}\ s^{-1}$;
$k_H = 1.48\,(\pm 0.19) \times 10^{-6}\ dm^3\ mol^{-1}\ s^{-1}$

3AP: $k_0 = 9.6\,(\pm 1.5) \times 10^{-8}\ s^{-1}$;
$k_H = 10.6\,(\pm 0.50) \times 10^{-6}\ dm^3\ mol^{-1}\ s^{-1}$

2AF: $k_0 = 0.67\,(\pm 0.32) \times 10^{-8}\ s^{-1}$;
$k_H = 3.35\,(\pm 0.10) \times 10^{-6}\ dm^3\ mol^{-1}\ s^{-1}$

As the intercepts, k_0, of eqn. (3) are subject to a large uncertainty, the 'spontaneous' (water-catalysed) rate constants, k_{H_2O}, were measured directly in water.

The results obtained are shown in Table 1.

Iodination of **2AP**, **3AP** *and* **2AF** *in Acetate Buffers.*—The rates of iodination of **2AP**, **3AP** and **2AF** were also studied in acetate buffers. Ketone concentrations ([S]) were varied over a wide range (1–4 × 10^{-2} mol dm^{-3}), but kinetic measurements were normally carried out with [S] *ca.* 2 × 10^{-2} mol dm^{-3}. The observed rate constants, k_e [eqn. (1)], were of the form shown in eqn. (4).

$$k_e = k_0 + k_{AcO}[AcO^-] \qquad (4)$$

Two sets of k_e values were measured for the three ketones at $r = [AcO^-]/[AcOH] = 1$ and 3, each set at six or more different concentrations of AcO^- in a range of *ca.* a factor of 10. The value of k_{AcO} is independent of the buffer ratio r, within the experimental error, and represents the second-order rate constant of the acetate-anion catalysed reaction (Table 1). There is no evidence of general acid catalysis by the acidic component of the buffer.

Each k_{AcO} value of Table 1 is an average of individual values determined in the two buffer systems (r = 1 and 3). Values of k_e calculated from eqn. (4) using experimental k_o and k_{AcO} values agree with experimental values to within 4%.

Bromination of **2AP**, **3AP** *and* **2AF** *in Dilute Sodium Hydroxide Solutions.*—Ionisation rates in dilute hydroxide solutions were too rapid to measure using zero-order conditions. The rates were measured instead under pseudo-first-order conditions[10] as rates of bromination [eqn. (2)] in solutions containing a slight excess of bromine as previously described.[4,11] The second-order rate constants obtained from eqn. (5) for

$$k_e = k_0 + k_{OH}[OH^-] \qquad (5)$$

reactions with hydroxide (k_{OH}) are reported in Table 1.

Values of k_e calculated from eqn. (5) using experimental k_0 and k_{OH} values agree with experimental values to within 10% in a range of hydroxide concentration 5–50 × 10^{-3}; 7.5–75 × 10^{-3} and 50–250 × 10^{-3} mol dm^{-3} for **2AP**, **3AP** and **2AF**, respectively.

Metal Ion Catalysed Iodination of **2AP**, **3AP** *and* **2AF**.—The effect of Cd^{2+}, Zn^{2+}, Ni^{2+} and Cu^{2+} on the rates of iodination of the three ketones was studied in unbuffered solutions (pH in the range 4–6). Substrate concentrations were *ca.* 2 × 10^{-2} mol dm^{-3} and the concentrations of I_2 and I^- were the same as those for reactions in the absence of metal ions. Ionic strength was 0.3 mol dm^{-3} for all reactions (KCl). Rates were measured at several metal ion concentrations in the range 2.5–75 × 10^{-3} mol dm^{-3}. In the case of Cu^{2+} the concentration range 0.25–7.5 × 10^{-3} mol dm^{-3} was chosen instead, in order to avoid precipitation of CuI_2.

The observed rate constants, k_e, of the form shown in eqn. (1) for **2AP** in the presence of Zn^{2+} and Ni^{2+} and for **2AF** in the presence of Cu^{2+} were (in the above range of concentration) essentially coincident, within experimental error, with the corresponding 'spontaneous' rate constants, k_{H_2O} (see Table 1). For the remaining metal ions and ketones, k_e showed a linear increase with increasing metal ion concentration according to eqn. (6), where $[M^{2+}]$ represents the molar concentration of

$$k_e = k_0 + k_M[M^{2+}] \qquad (6)$$

Cd^{2+}, Zn^{2+}, Ni^{2+} or Cu^{2+}. The plots of the k_e *vs.* the molar concentration of M^{2+} are linear, which shows that saturation is not occurring even at the highest used metal ion concentration. The results obtained are reported in Table 2. Values of k_e, calculated from eqn. (6), using k_0 and k_M values from Table 2 agree to within 8% of experimental values.

Zn^{2+} *Catalysed Iodination of* **2AP** *and* **3AP** *in Acetate Buffers.*—The effect of Zn^{2+} addition on the rate of the acetate catalysed iodination of **2AP** and **3AP** was also studied. Acetate ion concentrations were varied in the range 0.0075–0.20 mol dm^{-3} at a fixed Zn^{2+} concentration of 0.025 mol dm^{-3}. The following results were obtained:

2AP: $r = 1$
$k_e = 5.93\,(\pm 0.47) \times 10^{-8} + 6.86\,(\pm 0.41) \times 10^{-7}[AcO^-]$
$r = 3$
$k_e = 5.97\,(\pm 0.35) \times 10^{-8} + 6.59\,(\pm 0.37) \times 10^{-7}[AcO^-]$

3AP: $r = 1$
$k_e = 7.74\,(\pm 1.54) \times 10^{-6} + 2.46\,(\pm 0.14) \times 10^{-4}[AcO^-]$
$r = 3$
$k_e = 6.27\,(\pm 1.77) \times 10^{-6} + 2.66\,(\pm 0.18) \times 10^{-4}[AcO^-]$

Acetate concentrations were kept lower than those adopted in the absence of Zn^{2+} in order to avoid complexation[12] between the carboxylate ion and Zn^{2+}.

The above slope values, in the presence of 0.025 mol dm^{-3} Zn^{2+}, can be compared with the corresponding values (see Table 1) of $k_{AcO} = 6.39 \times 10^{-7}$ and 2.50×10^{-5} dm^3 mol^{-1} s^{-1} for **2AP** and **3AP**, respectively, showing that while Zn^{2+} leaves

Table 1 Catalytic constants (k/dm^3 mol^{-1} s^{-1}) for the enolisation of 2-acetyl-*N*-methylpyrrole (**2AP**), 3-acetyl-*N*-methylpyrrole (**3AP**), 2-acetylfuran (**2AF**), 2-acetylthiophene (**2AT**), 3-acetylthiophene (**3AT**) and acetophenone (**A**) at 25 °C and ionic strength 0.3 mol dm^{-3} (KCl or $NaClO_4$)

Acid or base	**2AP**	**3AP**	**2AF**	**2AT**[a]	**3AT**[a]	**A**
H_2O[b]	72.2 (±3.1) × 10^{-9}	154 (±6) × 10^{-9}	6.72 (±0.42) × 10^{-9}	2.00 (±0.16) × 10^{-9}	2.22 (±0.30) × 10^{-9}	4.11 (±0.20) × 10^{-9}[a]
Hydronium ion	1.48 (±0.19) × 10^{-6}	10.6 (±0.5) × 10^{-6}	3.35 (±0.10) × 10^{-6}	3.95 (±0.10) × 10^{-6}	11.8 (±0.2) × 10^{-6}	10.0 × 10^{-6}[c]
Acetate[d,e]	6.39 (±0.41) × 10^{-7}	250 (±19) × 10^{-7}	10.7 (±0.9) × 10^{-7}	5.80 (±0.44) × 10^{-7}	6.58 (±0.45) × 10^{-7}	8.4 (±0.3) × 10^{-7}[c]
Hydroxide ion	0.931 (±0.041)	0.159 (±0.006)	0.408 (±0.008)	0.275 (±0.015)	0.246 (±0.012)	0.24[f]

[a] See ref. 4. [b] Units are s^{-1}. [c] See ref. 11(*a*). [d] From k_e measured at $r = 1$ and 3. [e] For 2-acetylpyridine $k_{AcO} = 72.5\ (\pm 0.9) \times 10^{-7}$ dm^3 mol^{-1} s^{-1} and for 4-acetylpyridine $k_{AcO} = 335 \times 10^{-7}$ dm^3 mol^{-1} s^{-1} as reported in ref. 1. [f] See ref. 10.

Table 2 Metal ion catalysed iodination of **2AP**, **3AP**, **2AF**, **2AT**, **3AT** and **A** at 25 °C

Substrate	Catalyst	k_0/10^{-9} s^{-1}	k_M/10^{-8} dm^3 mol^{-1} s^{-1}
2AP	Cu^{2+}	56.1 (±1.3)	466 (±32)
	Cd^{2+}	57.8 (±6.0)	237 (±16)
3AP	Cu^{2+}	2 320 (±2 700)	788 000 (±64 000)
	Zn^{2+}	196 (±37)	3 200 (±100)
	Cd^{2+}	169 (±18)	757 (±46)
	Ni^{2+}	290 (±265)	31 800 (±1 000)
2AF	Zn^{2+}	3.61 (±0.11)	3.56 (±0.28)
	Cd^{2+}	3.72 (±0.32)	5.69 (±0.73)
	Ni^{2+}	2.52 (±0.33)	26.6 (±1.3)
2AT	Cu^{2+}	1.35 (±0.04)	23.5 (±1.0)
	Zn^{2+}	1.89 (±0.68)[a]	20.9 (±1.7)[a]
	Cd^{2+}	1.77 (±0.07)[a]	3.22 (±0.18)[a]
3AT	Cu^{2+}	1.47 (±0.04)	14.1 (±1.0)
	Zn^{2+}	0.47 (±1.00)[a]	19.0 (±2.5)[a]
	Cd^{2+}	1.47 (±0.11)[a]	2.73 (±0.28)[a]
A	Cu^{2+}	2.78 (±0.16)	28.4 (±3.8)
	Zn^{2+}	0.56 (±1.37)[a]	31.8 (±3.4)[a]
	Cd^{2+}	2.21 (±0.13)[a]	4.56 (±0.34)[a]

[a] Data from ref. 4.

Table 3 Metal activating factors (MAF) with reference to the proton (k_M/k_H) for the various acetyl heterocycles and acetophenone

Substrate	Catalyst	MAF
A	Cu^{2+}	0.028
	Zn^{2+}	0.032[a]
	Cd^{2+}	0.0046[a]
2AT	Cu^{2+}	0.059
	Zn^{2+}	0.053[a]
	Cd^{2+}	0.0082[a]
3AT	Cu^{2+}	0.012
	Zn^{2+}	0.016[a]
	Cd^{2+}	0.0023[a]
2AF	Zn^{2+}	0.011[a]
	Cd^{2+}	0.017[a]
	Ni^{2+}	0.079[a]
2AP	Cu^{2+}	3.1
	Cd^{2+}	1.6
3AP	Cu^{2+}	7.4 × 10^2
	Zn^{2+}	3.0
	Cd^{2+}	0.71
	Ni^{2+}	30

[a] Data from ref. 4.

k_{AcO} for **2AP** essentially unchanged, it increases k_{AcO} for **3AP** by approximately a factor of 10. This is in agreement with the results obtained in unbuffered solutions where Zn^{2+} behaves as an effective catalyst only towards **3AP**, but not towards **2AP** (Table 2). The same conclusion can also be arrived at by comparing the difference in the above intercepts for **2AP** and **3AP** with the corresponding difference in k_{H_2O} reported in Table 1.

^{13}C *NMR Spectra of* **3AP** *in the Presence of* Cu^{2+} *Ions*.—Addition of $Cu(NO_3)_2$ in the concentration range 0.04–0.4 mol dm^{-3} did not affect the ^{13}C NMR spectra of **3AP** in D_2O. Chemical shifts of the carbonyl carbon, the methyl carbon directly linked to the nitrogen atom and the methyl carbon adjacent to the carbonyl group remained essentially unchanged at 198.2, 35.95 and 25.90 ppm, respectively. The chemical shifts of the ring carbons remained unchanged, too. It should be recalled that **3AP** and the Cu^{2+} ion are the substrate and catalyst for which metal ion catalysis was found to be most effective (see the MAF values in Table 3). No evidence of complexation of **2AT** and **3AT** was previously[4] found by inspection of UV spectra in the presence of Zn^{2+} or Cd^{2+}.

Discussion

The present results as well as the relevant previous data[4] collected in Tables 1 and 2 show that the investigated ketones (**2AT**, **3AT**, **2AP**, **3AP**, **2AF** and acetophenone) are characterised by a large variability of relative reactivities depending upon the reaction conditions under which their enolisation reactions occur. The so called 'spontaneous' reactions show a tendency for **2AP** and (particularly) **3AP** to be considerably more reactive than the remaining ketones. The same is true for **3AP** in the acetate catalysed reaction where **3AP** is again some 30 times more reactive than acetophenone. This high reactivity of the acetylpyrroles can hardly be understood in terms of an electron-withdrawing effect of the heterocyclic ring which should make the methyl hydrogens of the acetyl group more easily removable by a base catalyst in the transition state of the enolisation reaction. From this point of view alone **2AF** should be the most reactive acetyl heterocycle in base-catalysed reactions. The idea of 'π-excessive'[9] aromatic compounds applied to pentatomic heterocycles as compared to benzene derivatives and the consequent electronic distribution in the ring carbon atoms is also of little help as, contrary to experimental evidence, acetophenone should be the most reactive substrate in base catalysed reactions.

The 'levelling off' effect previously observed[4] for the hydroxide catalysed reactions of **2AT** and **3AT** is fully confirmed, k_{OH} values for the investigated ketones ranking within a factor of less than six, **2AP** being the most reactive substrate in this very fast reaction. In the specific acid catalysed reaction **3AP**, **3AT**[4] and acetophenone are nearly equally reactive and considerably more reactive than **2AT**,[4] **2AF** and **2AP** (see Table 1). This might be due to the electron-withdrawing effect of the heteroatom which makes 3-acetyl derivatives relatively more basic than their 2-acetyl counterparts. Indeed, the accepted mechanism for the acid-catalysed process[13] involves a pre-equilibrium proton transfer to the carbonyl group, with subsequent C–H ionisation being assisted by water or the conjugate base of the acid catalyst.

Previous studies[4] of the metal ion effects on the rates of enolisation of **2AT**, **3AT** and acetophenone evidenced pronounced accelerations by Cd^{2+} and Zn^{2+} (not by Ni^{2+}) even though the measured MAF values were relatively small as mentioned in the introduction.

The new investigated substrates and metal ions display in some instances dramatic effects (see Table 2). For example, Cu^{2+} *is ca.* 740 *times* more effective than the proton in promoting the enolisation of **3AP**. MAF values (expressed with reference to the proton) are all close to or higher than one for **2AP** and **3AP** as reported in Table 3. There is no evidence of a bidentate coordination of nitrogen and oxygen atoms of **2AP** by the different metal ions, as the MAF values found for **2AP** are close to or lower than those observed for the corresponding reactions of **3AP**, where chelation is not possible.

The observed rate accelerations can generally be attributed to the participation of the metal cations in stabilising the transition states of the enolisation reactions as previously suggested.[4] The kinetically equivalent enhanced reactivity of a certain amount of the reacting ketone complexed by the metal ion seems unlikely. Indeed, there is no direct evidence of such complexation, while the partial negative charge generated on the carbonyl oxygen should allow relatively stronger metal ion binding in the transition state. Water molecules will also be ligated to the metal ion and will be moderately acidic. Therefore general acid catalysis by metal ion bound water might be an alternative explanation of the observed effects. However, this also seems unlikely as the pK_a values of aquo-complexes[14] of such metal ions as Cu^{2+}, Zn^{2+} and Ni^{2+} are 6.8, 8.8 and 10.6, respectively, while general acid catalysis by acetic acid was not observed (see Results) and was previously detected[4] only for carboxylic acids stronger than mandelic acid ($pK_a = 3.41$). Replacement of a water ligand on the metal ion must occur during the enolisation process and the strength of binding in the transition state must be of critical importance with regard to the magnitude of the metal ion effect. A much higher electron density on the carbonyl oxygen atoms of **2AP** and **3AP** as compared to the other investigated aromatic ketones is the probable origin of the high MAF values observed for **2AP** and **3AP** (Tables 2 and 3).

This would be in agreement with the conclusion[15] recently derived from ^{17}O NMR chemical shifts that there is an exceptionally high electronic density on the carbonyl oxygen atom of acetyl-*N*-methylpyrroles (505.4 and 509.4 ppm in acetonitrile for **2AP** and **3AP**, respectively) as compared to acetylfuran (525.6), acetylthiophenes (528.1 and 539.1 ppm for **2AT** and **3AT**, respectively) and acetophenone (548.6 ppm).[16]

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