Equilibrium Constants for Ionisation and Enolisation of 3-Nitrobutan-2-one

Antonella Fontana,*[a] Paolo De Maria,[a] Gabriella Siani,[a] Marco Pierini,[a]
Simona Cerritelli,[a] and Roberto Ballini[b]

Keywords: Tautomerism / Ketones / Kinetics / Ionisation / Semiempirical calculations

The equilibrium constant for the keto-enol tautomerism of 3-nitrobutan-2-one K_T = [enol]/[ketone] has been measured in water as 4.57×10^{-3} ($pK_T = 2.34$) by combining the rate constants for ketonisation of the enolate form and pK_a of the ketone at 25 °C. The rates of ketonisation were measured by a rapid kinetic technique and the pK_a was determined spectrophotometrically and potentiometrically as 5.15. A comparison with 2-butanone and acetone shows a strong influence of the nitro group in enhancing the acidity of the substrate and in stabilizing the enol relative to the keto tautomer. By means of semiempirical AM1 calculations, good correlations were found between the atomic charge on the acidic hydrogens and the pK_a (in water at 25 °C) of both tautomeric forms for a number of simple ketones whose pK_as and pK_Ts are available in the literature. The agreement of experimental acidity constants of the enol, pK_a^{EH}, the ketone, pK_a^{KH}, and the tautomeric constant, pK_T, with predicted values is satisfactory.

Introduction

There have been several recent investigations[1–6] on keto-enol interconversion and determinations of the tautomerisation equilibrium constants, K_T, by combining the rate constants for enolisation and ketonisation in basic aqueous solutions. The substrates studied so far were generally acidic enough to be (about 10–20%) ionised in relatively dilute (0.5 mol dm^{-3}) NaOH in order to follow the ketonisation reaction of the enol form accurately by stopped-flow techniques. α-Nitro ketones are acid ketones; it has long been known[7] that, for example, nitroacetone has a pK_a of about 5 and this value can be compared with that of acetone ($pK_a = 19.16$).[8] However, kinetic studies on the tautomerism of nitro ketones are scarce.[2,9] The enol content for simple derivatives is believed[10] to be very low but "the paucity of the data do not make it possible to examine structural effects on the enol content of α-nitro ketones in detail."[2] α-Nitro ketones are, in principle, an equilibrium mixture of the tautomeric forms shown in Scheme 1:

a	b	c
$RCOCH(NO_2)R'$	$RC(OH){=}C(NO_2)R'$	$RCOC(R'){=}NO_2H$
keto form	enol form	aci form

Scheme 1. Tautomeric forms of 3-nitrobutan-2-one

It is considered[2,11] that **c** can generally be neglected for practical purposes, probably due to the high acidity of the aci form in aqueous solutions.

Ab initio studies[12] on α-substituted acetaldehydes have shown that electron-withdrawing groups such as the nitro group destabilize the keto form **a** and stabilize the enol form **b** by electron delocalization and, possibly, by H-bonding. The enol form is also favoured by apolar solvents, while polar solvents generally favour the keto form, probably due to its higher dipole moment.[13,14] Furthermore, for example, the keto form of α-nitrocyclohexanone is destabilized[10] by steric hindrance between the substituent and the carbonyl group, as well as by electrostatic repulsion between the two polar functionalities.

With this work we have measured the rates of ketonisation of the enolate of 3-nitrobutan-2-one as well as the pK_a of the keto form in water at 25.0 ± 0.1 °C. From the obtained results the pK_a of the enol and the keto-enol tautomerisation constant K_T could be derived.

We have also performed some AM1 semiempirical calculations of the atomic charge located on the acidic hydrogens of both the keto and the enol forms of 3-nitrobutan-2-one and some related ketones and enols of known pK_a (in water). The charge density values have been correlated with pK_as for both tautomers. Experimental and calculated values have been compared.

Results

Ketonisation Reactions in Aqueous Buffers

The rates of ketonisation of the enolate of 3-nitrobutan-2-one have been measured in chloroacetate, glycolate, and acetate buffers at different buffer ratios, $r = [A^-]/[HA]$. The concentration of A^-, the conjugate base of the buffer acid HA, was varied over the range $0.6–6 \times 10^{-2}$ mol dm^{-3} at each buffer ratio. In all cases the observed pseudo-first order rate constants k_e were measured at different concentrations (in the range $5–400 \times 10^{-3}$ mol dm^{-3}) of $NaHSO_3$

---

[a] Dipartimento di Scienze del Farmaco,
Università 'G. D'Annunzio',
Via dei Vestini 31, 66013 Chieti, Italy
Fax: (internat.) + 39-0871/355-5204
E-mail: fontana@unich.it, demaria@unich.it
[b] Dipartimento di Scienze Chimiche, Università di Camerino,
Via S. Agostino 1, 62032 Camerino (Macerata), Italy
E-mail: ballini@camserv.unicam.it

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/eurjoc or from the author.

1434−193X/00/0408−1641 $ 17.50+.50/0

as the scavenger[15,16] of the keto form (see Experimental Section). The k_e values (see Table 1) showed an increase with increasing [$NaHSO_3$] at low concentration of $NaHSO_3$, but levelled off to a limiting value at higher concentration (Table 1 and Supplementary Material: Table S1).

Table 1. First order rate constants (k_e) for the reaction of 3-nitrobutan-2-one with bisulfite ion in acetate buffer (r = 1, [AcO^-] = 0.03 mol dm^{-3}) at 25 °C and ionic strength 0.4 mol dm^{-3}

[HSO_3^-]/mol dm^{-3}	k_e/10^{-1} s^{-1}
0.020	0.699
0.030	0.805
0.050	0.915
0.070	1.026
0.100	1.117
0.125	1.208
0.150	1.274
0.170	1.246
0.200	1.281

In the "plateau" region the reaction is zero-order in $NaHSO_3$, showing that the ketonisation step becomes rate-determining and that $NaHSO_3$ indeed performs as a good scavenger of the keto form of 3-nitrobutan-2-one. Under these conditions the "plateau" value k'_e is linearly related to the molar concentration of HA by Equation (1).

$$k'_e = k_o + k_{HA}\,[HA] \qquad (1)$$

Table 2. Slopes, k_{HA}, and intercepts, k_o, from the plot of the experimental pseudo-first order rate constants (k_e/s^{-1}) of ketonisation of the enolate of 3-nitrobutan-2-one against concentration of buffer acid in aqueous solution at 25 °C and ionic strength 0.4 mol dm^{-3}

Buffer	r	pH_{exp}	k_o/s^{-1}	k_{HA}[a] / dm^3 mol^{-1} s^{-1}
Chloroacetate	0.5	2.88	0.101 (±0.007)	4.96 (±0.17)
	3	3.12	0.072 (±0.002)	5.67 (±0.14)
	5	3.43	0.059 (±0.002)	5.79 (±0.29)
Glycolate	1	3.61	0.063 (±0.002)	2.49 (±0.07)
	3	3.99	0.050 (±0.001)	3.23 (±0.06)
	5	4.45	0.047 (±0.001)	3.19 (±0.15)
Acetate	0.5	4.18	0.051 (±0.002)	1.52 (±0.03)
	1	4.42	0.051 (±0.001)	1.52 (±0.01)

[a] The concentrations of buffer acid used to calculate k_{HA} values have been corrected allowing for the dissociation of the acid at the experimental pH values and the ionic strength of the solutions.

The buffer-independent rate constants k_o are reported in Table 2 together with the corresponding pH values of the solutions. The values of k_{HA} (Table 2) are essentially independent of the buffer ratios r for glycolate and acetate buffer systems. The (about 16%) increase of k_{HA} for chloroacetate buffer on passing from r = 0.5 to r = 5 can be accounted for by an incomplete correction of the dissociation of this relatively strong acid in terms of activity coefficients (see footnote of Table 2). We can therefore conclude that k_{HA} values represent the general acid-catalysed contribution by the undissociated buffer acid HA [Brønsted α = 0.29 from a plot of log k_{HA} *vs* log ($1/K_a$)]. No general base contribution by the conjugate base A^- was observed as expected for the reaction of a negatively charged substrate with an anionic catalyst.

Ketonisation Reactions in Dilute Hydrochloric Acid and pH Profile

The pseudo-first-order ketonisation rate constants k'_e were similarly measured at different concentrations of HCl (in the range 9–151 × 10^{-4} mol dm^{-3}) and with $NaHSO_3$ concentrations within the "plateau" region. The obtained results are reported in Table 3. By using k_o values from Table 2, k'_e values from Table 3 and the corresponding experimental pH values, the pH-profile diagram shown in Figure 1 could be drawn.

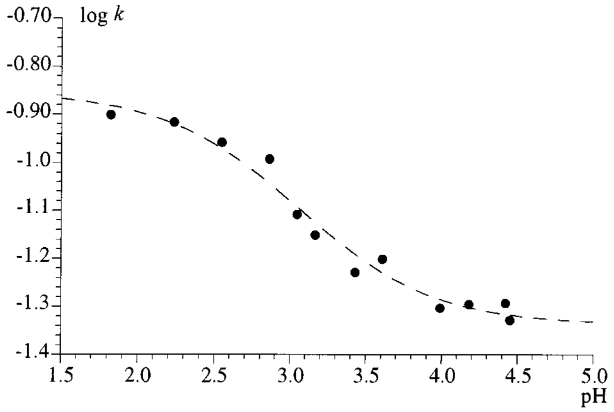


Figure 1. pH-Profile for the ketonisation reactions of the enolate of 3-nitrobutan-2-one; the k values are either the buffer-independent rate constants, k_o of Equation (1), measured in the different buffers, or the experimental k'_e values determined in dilute HCl solutions; pH values are those measured experimentally in the different solutions

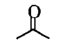
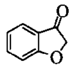
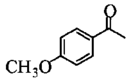
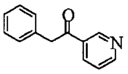
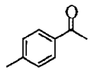
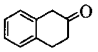
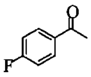
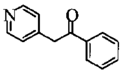
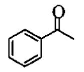
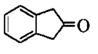
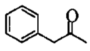
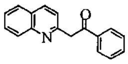
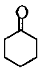
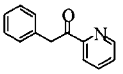
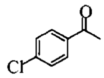
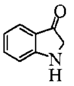
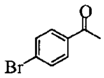
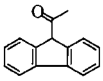
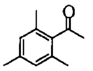
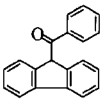
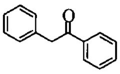
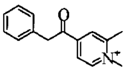
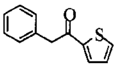
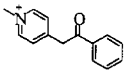
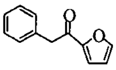
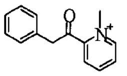
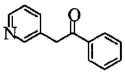
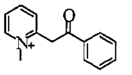
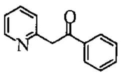
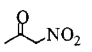
Table 3. Pseudo-first order rate constants (k'_e) for the ketonisation of the enolate of 3-nitrobutan-2-one in HCl at 25 °C and ionic strength 0.4 mol dm^{-3}

[HCl]/10^{-2} mol dm^{-3}	pH_{exp}	k'_e/s^{-1}
0.0900	3.05	0.078 (±0.001)
0.284	2.55	0.110 (±0.002)
0.583	2.23	0.121 (±0.002)
1.51	1.82	0.126 (±0.002)

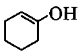
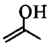
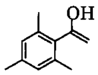
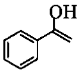
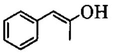
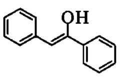
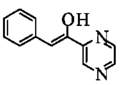
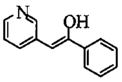
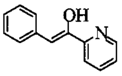
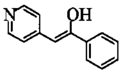
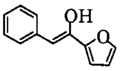
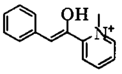
Semiempirical Calculations

The adopted procedure for performing the calculations mentioned in the Introduction was as follows: (i) Only monocarbonyl compounds with known pK_as (in water) for both tautomeric forms were chosen; (ii) Preliminary structure optimisations, search for conformations and optimisation of their geometries were performed by molecular mechanics; (iii) Only conformers within 3 kcal mol^{-1} from the minimum were selected; (iv) Further optimisation of the geometries of the selected conformations was achieved by the AM1 semiempirical method; (v) Charge densities on the

Table 4. Compounds selected for the semiempirical calculations; (a) keto form, (b) enol form

N.	Keto form	pK_a^{KH}	Ref.	N.	Keto form	pK_a^{KH}	Ref.
1		19.27	[1]	16		13.22	[1]
2		18.90	[1]	17		13.20	[1]
3		18.80	[1]	18		12.90	[1]
4		18.40	[1]	19		12.58 [a]	[1]
5		18.31	[1]	20		12.20	[1]
6		18.24	[1]	21		12.20	[1]
7		18.09	[1]	22		12.05	[24]
8		18.00	[1]	23		11.52	[1]
9		17.90	[1]	24		9.94	[1]
10		17.61	[1]	25		9.44	[1]
11		14.75	[23]	26		9.02	[1]
12		14.60	[1]	27		7.58	[1]
13		14.40	[5]	28		6.90	[24]
14		13.70	[1]	29		6.64 [a]	[1]
15		13.27	[1]	30		5.10	[25]

[a] Averaged value of literature data.

N.	Enol form	pK_a	Ref.
1		11.7	[1]
2		10.94	[1]
3		10.69	[1]
4		10.34	[1]
5		10.34	[1]
6		9.6	[23]
7		9.0	[26]
8		8.83	[1]
9		8.75	[24]
10		8.5	[1]
11		8.5	[5]
12		5.9	[24]

acidic hydrogens were averaged in terms of the Boltzmann probability of each conformation.

The calculated atomic charges for the compounds of Table 4(a) and Table 4(b) were plotted against their literature pK_a values. The obtained linear correlations

$$\text{charge (keto form)} = -0.004\ pK_a^{KH} + 0.1817$$

$$\text{charge (enol form)} = -0.0072\ pK_a^{KH} + 0.2934$$

are shown in Figure 2(a) and Figure 2(b), respectively. Correlation coefficients are: r (ketones, 2a) = 0.973; r (enols, 2b) = 0.951. Standard pK errors are: pK_a^{KH} (ketones) = ±0.97; pK_a^{EH} (enols) = ±0.50. The validation plot of calculated against experimental pK_T values has a correlation coefficient r = 0.927 and a standard error of ±0.85 (Figure 3).

Discussion

The pH-profile for the ketonisation reaction (see Figure 1) shows a pH region for apparent H_3O^+ catalysis ($2.5 \leq pH \leq 3.5$) and two regions where the reaction becomes pH-independent. The pH-independent region at higher pH is probably due to the complete ionisation of the enol to the enolate anion and its subsequent reaction with water to give the ketone. The curve at intermediate pH represents the H_3O^+ catalysed reaction of the enolate according to Scheme 2.

The pH-independent region at lower pH corresponds to the complete conversion of the enolate to the enol form. A contribution of H_3O^+ catalysis to the ketonisation reaction of the undissociated enol was not detected in the investig-

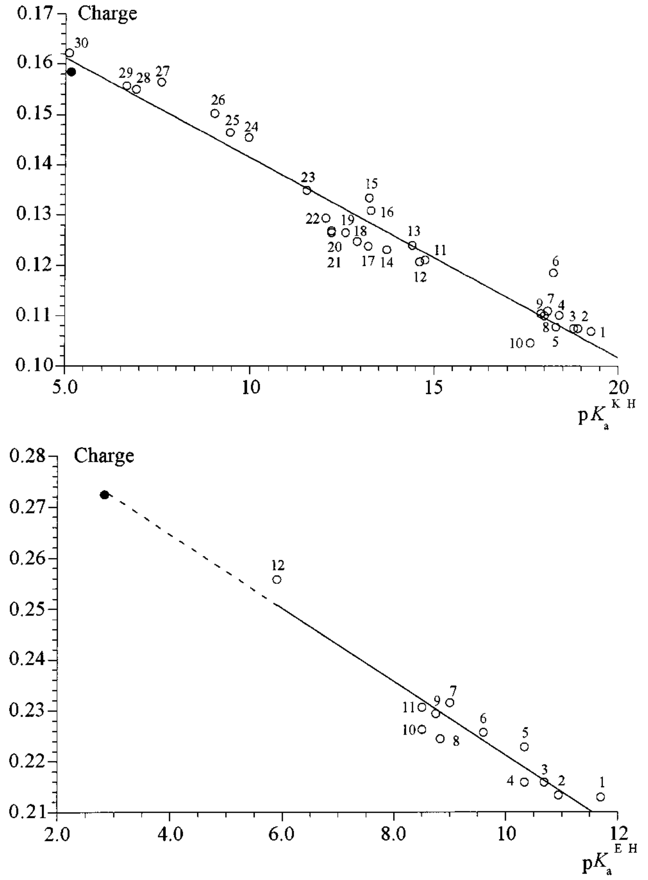


Figure 2. Linear relationship between charge density and pK_a for both the keto (upper plot) and the enol (lower plot) forms; open and full symbols refer to compounds reported in Table 4 and 3-nitrobutan-2-one, respectively.

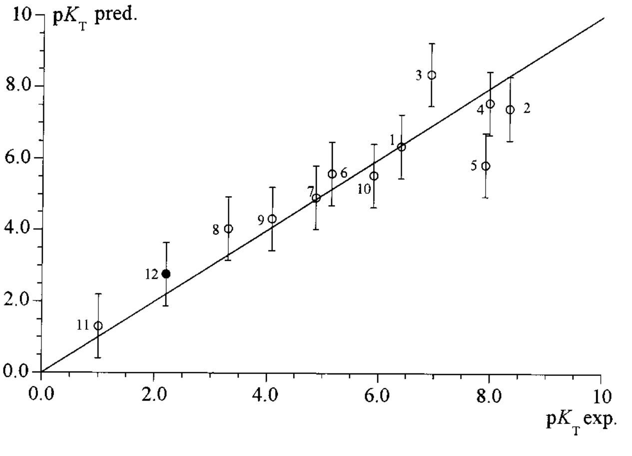
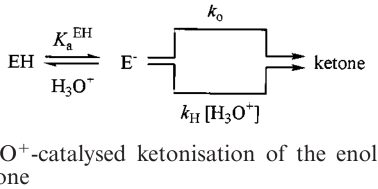


Figure 3. Validation plot of calculated against experimental pK_T values for compounds reported in Table 5; full symbol refers to 3-nitrobutan-2-one.



Scheme 2. H_3O^+-catalysed ketonisation of the enolate (E^- of 3-nitrobutan-2-one

ated range of pH values as it is known[1] that such a contribution is detectable only at higher H_3O^+ concentrations for very acidic enols.

As the H_3O^+ catalysed reaction of the enolate E^- is kinetically indistinguishable from the "water" reaction of the enol EH, rate constants for the "water" ketonisation of the enolate, $k_o^{E^-} = 0.046\ s^{-1}$, and of the enol, $k_o^{EH} = 0.140\ s^{-1}$, and a value of the acidity constant of EH, $pK_a^{EH} = 2.81 \pm 0.10$, could be obtained from the best fit of experimental data to the sigmoid curve of Figure 1 by means of Equation (2).

$$k = \frac{k_o^{E^-} + k_H^{E^-}[H^+]}{1 + ([H^+]/K_a^{EH})} \tag{2}$$

where $k_H^{E^-} = k_o^{EH}/K_a^{EH}$. Owing to the fact that the independently measured $pK_a^{apparent} = 5.15$ (average value obtained by the spectrophotometric and potentiometric methods described in the Experimental Section) turned out to be much higher than pK_a^{EH}, the influence of the enol in the determination of the pK_a^{KH} is negligible and the above value of $pK_a^{apparent}$ can be taken as coincident with the value of pK_a^{KH}. It is interesting that this value of pK_a^{KH} is considerably lower than those of typical β-diketones such as acetylacetone ($pK_a^{KH} = 8.84$)[17] and indandione ($pK_a^{KH} = 7.41$ in 1% methanol/99% water mixture).[18]

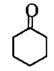
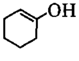
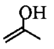
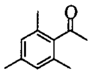
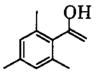
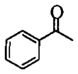
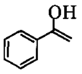
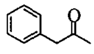
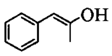
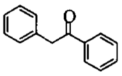
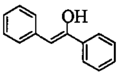
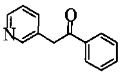
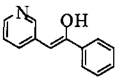
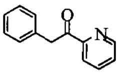
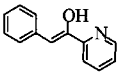
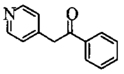
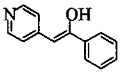
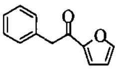
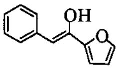
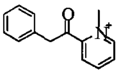
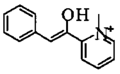
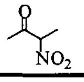
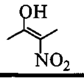
By combining pK_a^{KH} and pK_a^{EH} the value of the tautomeric constant of 3-nitrobutan-2-one ([enol]/[ketone] = 4.57×10^{-3}; $pK_T = 2.34$) can finally be obtained. This value is lower than that reported for 2-butanone ($pK_T = 7.50$),[19] showing that the presence of a nitro substituent, for the reasons mentioned in the Introduction, effectively increases the amount of enol in the tautomeric equilibrium of a simple ketone.

Our semiempirical calculations provide a method for predicting the acidities (pK_a in water) of the keto and enol forms of simple monocarbonyl ketones. This method is based on the determination of the atomic charge density located on the acidic hydrogen of the substrate by following the steps illustrated in the Results section. Figure 2 shows that a good linear relationship exists between charge density and pK_a for both the keto [Figure 2(a)] and enol [Figure 2(b)] forms. The validation curve of calculated pK_T values (according to the equation: $pK_T = pK_a^{KH} - pK_a^{EH}$) against literature pK_T values also shows a good correlation (Figure 3).

We conclude that the proposed semiempirical approach is of some general use in predicting pK_a values of simple ketones and enols which are experimentally not easily accessible in water, as well as the corresponding tautomeric constants pK_T.

The experimental results obtained for 3-nitrobutan-2-one (Table 5) can be used to test the validity of our approach. A comparison of the predicted and experimental values $\Delta pK_a^{KH} = 0.67$, $\Delta pK_a^{EH} = 0.10$, $\Delta pK_T = 0.57$ is satisfactory and provides additional confidence on the semiempirical method.

Table 5. Comparison of predicted and experimental equilibrium constants for ionisation and keto-enolisation of selected ketones and 3-nitrobutan-2-one

N.	Keto form (KH)	pK_a Exp.	pK_a Pred.	ΔpK_a |E-P|	Enol form (EH)	pK_a Exp.	pK_a Pred.	ΔpK_a |E-P|	pK_T Exp.	pK_T Pred.	ΔpK_T |E-P|
1		18.09	17.55	0.54		11.7	11.19	0.51	6.39	6.36	0.03
2		19.27	18.55	0.72		10.94	11.13	0.19	8.33	7.42	0.91
3		17.61	19.13	1.52		10.69	10.76	0.02	6.92	8.37	1.45
4		18.31	18.33	0.02		10.34	10.76	0.42	7.97	7.57	0.40
5		18.24	15.65	2.59		10.34	9.81	0.53	7.90	5.84	2.06
6		14.75	15.00	0.25		9.6	9.41	0.19	5.15	5.59	0.44
7		13.70	14.50	0.08		8.83	9.58	0.75	4.87	4.92	0.05
8		12.05	12.93	0.88		8.75	8.89	0.14	3.30	4.04	0.74
9		12.58	13.65	1.07		8.5	9.33	0.83	4.08	4.32	0.24
10		14.40	14.28	0.12		8.5	8.74	0.24	5.90	5.54	0.36
11		6.90	6.53	0.37		5.9	5.23	0.67	1.00	1.30	0.30
12		5.15	5.82	0.67		2.81	2.91	0.10	2.34	2.91	0.57

Experimental Section

Instruments: The kinetic experiments were carried out with a Jasco V-550 UV/Vis spectrophotometer equipped with a Hi-tech rapid kinetic accessory for the faster reactions or with a Varian Cary 1E spectrophotometer. A 93 Radiometer pH-meter was used for the potentiometric titrations and pH measurements.

Materials: All inorganic salts [NaCl, $NaHSO_3$] were samples of AnalaR grade (Aldrich, Merck or Carlo–Erba) and were used without further purification. 3-Nitrobutan-2-one was prepared and purified according to reported methods.[20,21]

UV/Vis Spectra: The UV spectrum of an aqueous solution of 3-nitrobutan-2-one (about 5×10^{-5} mol dm^{-3}) shows an intense absorption band ($\lambda_{max} = 315$ nm) which slowly disappears after 24 h, presumably due to the hydration reaction of the ketone. This absorption band strongly increases in alkaline solution (NaOH $> 1 \times 10^{-4}$ mol dm^{-3}) while it immediately disappears upon acidification. In cyclohexane as a solvent this same band is absent. The above results suggest that the absorbing species in aqueous solution is the enolate of 3-nitrobutan-2-one, while the enol and keto forms apparently do not absorb in the same region.

Chemical Tests

Halogen Test: Upon addition of an I_2/I_3^- (or Br_2/Br_3^-) solution to a freshly prepared aqueous solution of excess 3-nitrobutan-2-one, the dark violet colour of I_3^- (or the reddish colour of Br_3^-) suddenly disappears suggesting that the substrate is present, to some extent, in its enol and/or enolate form.

$FeCl_3$ Test: This test is specific for enols and aci forms. The experiment was performed following a described procedure[22] and gave a positive response, confirming the results of the halogen tests.

Ionisation Constant: The ionisation constant K_a^{KH} of 3-nitrobutan-2-one in aqueous solution was determined spectrophotometrically at $\lambda = 315$ nm in glycolate, acetate, phosphate and borate buffers of different buffer ratios. The obtained value is, in principle, an "apparent" equilibrium constant due to the possible contribution of the dissociation of the enol form. A value of $pK_a^{apparent} = 5.12 \pm 0.15$ was obtained as the intercept of the straight line of a $-\log I$ *vs* pH plot, where $I = (A_{max} - A)/A$ and A and A_{max} are the absorbances of equimolar solutions of 3-nitrobutan-2-one at the specified wavelength in the above buffer systems, and of the fully ionised ketone, respectively. The value of $pK_a^{apparent}$ was also determined potentiometrically by titrating an aqueous 10^{-2} mol dm^{-3} solution of 3-nitrobutan-2-one with standardized 10^{-1} mol dm^{-3} NaOH. The potentiometrically measured value, $pK_a^{apparent} = 5.19 \pm 0.15$ is in satisfactory agreement with that measured spectrophotometrically.

Kinetic Measurements: The rate of ketonisation of the enolate form of 3-nitrobutan-2-one was measured by using $NaHSO_3$ as the "scavenger" of the ketone following a previously described procedure.[15,16] The disappearance of the absorption of the enolate at 315 nm was followed for at least three half-lives at 25.0 ± 0.1 °C in different buffer solutions and in hydrochloric acid at a constant ionic strength of 0.4 mol dm^{-3} (NaCl).

The pH of the solution was measured before and after each experiment. A few microlitres of 3-nitrobutan-2-one sampled from a relatively concentrated stock solution in anhydrous dioxane were directly added to the cuvette immediately before the experiment in order to minimize the hydration of the substrate. The initial concentration of 3-nitrobutan-2-one was about 10^{-3} mol dm^{-3} in all experiments.

Semiempirical Calculations: Semiempirical calculations were performed on 30 keto and 12 enol forms whose pK_a values (in water) are available in the literature [Table 4(a) and Table 4(b)]. All molecular mechanics calculations were performed with the MM2 force field. A conformational search was carried out by the Monte Carlo stochastic algorithm on internal coordinate system and the minimisation method was the PR conjugate gradient as implemented by the MACROMODEL v. 4.5 program.

The selected conformations (i.e. within 3 kcal mol^{-1} from the global minimum) were optimised by a semiempirical calculation using the MOPAC v. 6.0 program and the following keywords: AM1 EF GNORM = 0.001 GEO-OK. Coulson's charge densities were averaged in terms of the Boltzmann probability (at 25 °C) of each conformation.

Acknowledgments

We wish to thank MURST (ex 60%) for financial support.

---

[1] J. R. Keefe, A. J. Kresge, in *The Chemistry of Enols* (Ed.: Z. Rappoport), Wiley Sons, New York, **1990**, 399.
[2] J. Toullec, in *The Chemistry of Enols* (Ed.: Z. Rappoport), Wiley Sons, New York, **1990**, 323.
[3] A. J. Kresge, *Acc. Chem. Res.* **1990**, *23*, 43.
[4] B. Capon, B.-Z. Guo, F. C. Kwok, A. P. Siddharta, C. Zucco, *Acc. Chem. Res.* **1988**, *21*, 135.
[5] A. Fontana, R. A. More O'Ferrall, *J. Chem. Soc., Perkin Trans 2*, **1994**, 2453.
[6] P. De Maria,A. Fontana, G. Cerichelli, *J. Chem. Soc., Perkin Trans 2*, **1997**, 2329.
[7] R. G. Pearson, R. L. Dillon, *J. Am. Chem. Soc.* **1953**, *75*, 2439.
[8] Y. Chiang, A. J. Kresge, Y. S. Tang, J. Wirz, *J. Am. Chem. Soc.* **1984**, *106*, 460.
[9] R. P. Bell, R. R. Robinson, *Proc. Roy. Soc. A*. **1962**, *270*, 411.
[10] T. Simmons, R. F. Love, K. L. Kreuz, *J. Org. Chem.* **1966**, *31*, 2400.
[11] A.T. Nielsen, in *The Chemistry of the Nitro and Nitroso Groups*, (Ed.: H. Feuer) Wiley Sons, New York, **1969**, 349.
[12] W. J. Bouma, L. Radom, *Aust. J. Chem.* **1978**, *31*, 1649.
[13] J. Emsley, N. J. Freeman, *J. Mol. Struct.* **1987**, *161*, 193.
[14] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Verlag Chemie, Weinheim, 2nd ed., **1988**.
[15] M. P. Harcourt, R. A. More O' Ferrall, *Bull. Soc. Chim. Fr.* **1988**, 407.
[16] M. P. Harcourt, R. A. More O' Ferrall, *J. Chem. Soc., Perkin Trans 2* **1995**, 1415.
[17] H. Koshimura, T. Okubo, *Anal. Chim. Acta* **1970**, *49*, 67.
[18] E. Y. Gren, G. Y. Vanag, *Zh. Org. Khim.* **1965**, *1*, 3.
[19] J. R. Keeffe, A. J. Kresge, N. P. Schepp, *J. Am. Chem. Soc.* **1990**, *112*, 4862.
[20] R. Ballini, G. Bosica, M. Parrini, *Tetrahedron Lett*. **1998**, *39*, 7963.
[21] G. Rosini, R. Ballini, M. Petrini, E. Marotta, P. Righi, *Org. Prep. Proc. Int.* **1990**, *22*, 707.
[22] R. M. Roberts, J. C. Gilbert, S. F. Martin, *Experimental Organic Chemistry*, Saunders College Publishing, **1994**, Chapter 23, 698.
[23] A. R. E. Carey, S. Eustace, R. A. More O'Ferrall, B.A. Murray, *J. Chem. Soc., Perkin Trans 2* **1993**, 2285.
[24] G. M. Mc Cann, Ph. D. thesis, University College Dublin, **1990**.
[25] E. S. Lewis, in *The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives*, Supplement F, Part 2 (Ed.: S. Patai), Wiley Sons, Interscience, **1982**, 717.
[26] A.-G. Collot, S. Eustace, R. A. More O'Ferrall, unpublished result.

Received October 20, 1999
[O99583]