Characterization of the indan-1-one keto–enol system

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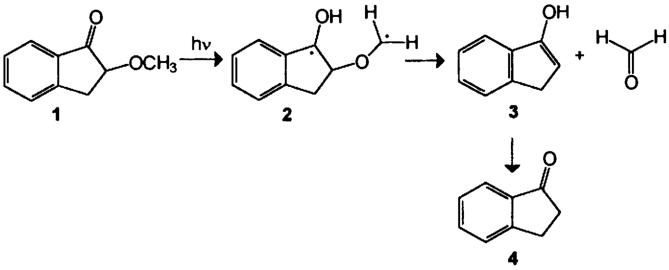
3-Hydroxyindene was generated by Norrish type II photoelimination of 2-methoxyindan-1-one, and its subsequent rate of ketonization was measured in dilute aqueous perchloric acid, sodium hydroxide, acetic acid buffer and ammonia buffer solutions. These data, when combined with acid-catalysed rates of enolization of indan-1-one determined by both bromine and iodine scavenging, give $pK_E = 7.48$ for the keto–enol equilibrium constant, $pK_a^E = 9.48$ for the acidity constant of the enol ionizing as an oxygen acid, and $pK_a^K = 16.96$ for the acidity constant of the ketone ionizing as a carbon acid. These results are compared with corresponding values for the acetophenone keto–enol system, using the redetermined acetophenone enol acidity constant, $pK_a^E = 10.40$, obtained here from rates of ketonization of the enol in sodium hydroxide and ammonia buffer solutions. All the present equilibrium constants refer to wholly aqueous solution at 25 °C and ionic strength = 0.10 mol dm^{-3}.

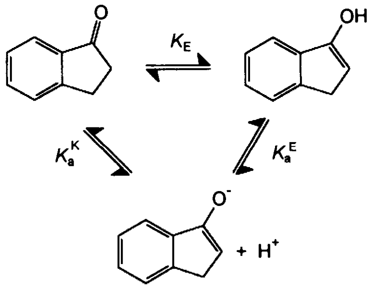
The chemistry of enols is of mechanistic as well as biological interest, and the evaluation of structural effects on keto–enol equilibrium constants, enol acidity constants, and ketone acidity constants is consequently of fundamental importance.[1] Keto–enol equilibrium constants of simple carbonyl compounds are generally too small to be determined directly, but accurate values may be obtained as ratios of enolization to ketonization rate constants: $K_E = k_E/k_K$. Values of k_E are easily determined by scavenging the enol as it is formed from the keto isomer, but the measurement of k_K is more challenging as it requires the generation of the usually short-lived enol in a greater than equilibrium concentration under conditions where its rate of ketonization can be determined accurately.

Enols can be generated by the well-known Norrish Type II reaction,[2] and this has been employed to study acetophenone enol,[3] ring-substituted acetophenone enols,[4] and the enols of acetaldehyde and acetone.[5] We report herein that this method can be used to generate the enol of indan-1-one (**4**), 3-hydroxyindene (**3**), flash photolytically from 2-methoxyindan-1-one (**1**), and that its subsequent ketonization kinetics can be monitored accurately by UV spectroscopy. Photoexcitation of the ketone leads to γ-hydrogen abstraction, diradical (**2**) formation, and disproportionation to afford 3-hydroxyindene and formaldehyde (Scheme 1).



Scheme 1

We have carried out a kinetic study of the indan-1-one keto–enol system which provides a comparison with the well-studied acetophenone system (Scheme 2).[3,6] The stabilizing effect of a fused *versus* an unfused α-phenyl substituent on enol chemistry is assessed. The measurement of rates of enolization of indan-1-one, k_E, as well as measurement of rates of ketonization of 3-hydroxyindene, k_K, provide an accurate value of the keto–enol equilibrium constant, K_E. Rate measurements in basic solution give a value for the acidity constant, K_a^E, of indan-1-one enol ionizing as an oxygen acid, and that, in combination with the keto–enol equilibrium constant, provides the acidity constant, K_a^K, of indan-1-one enol ionizing as a carbon acid. In addition, we have determined the pK_a^E of acetophenone enol by an accurate kinetic method; a pK_a^E value was obtained previously by spectrophotometric titration.[3b]



Scheme 2

Experimental

Materials

2-Methoxyindan-1-one was prepared in three steps from indan-1-one, by reported literature procedures.[7] α-Bromostyrene and phenylacetylene were distilled prior to use and indan-1-one was recrystallized from hexane for the enolization kinetic studies. All other materials were best available commercial grades.

Kinetics, ketonization

Reactions were initiated flash photolytically using a conventional flash-lamp system, which has been described previously.[5b] Substrate concentrations in the reaction mixtures were *ca.* 1 × 10^{-4} mol dm^{-3}. Ionic strength was maintained at 0.1 mol dm^{-3} with the use of $NaClO_4$. The reaction temperature was controlled at 25.0 ± 0.1 °C, with the use of a jacketed cell, by water circulating from an external constant temperature bath.

Concentrations of transient enols were monitored spectrophotometrically. The data obtained conformed well to the first-order rate law, and observed first-order rate constants were evaluated by least-squares fitting of an exponential function.

Kinetics, enolization

Rates of acid-catalysed enolization of indan-1-one were measured using both bromine and iodine to scavenge

3-hydroxyindene. Bromine scavenging rates were determined in the presence of bromide ion using the absorbance of Br_3^-, at λ = 320 nm, to monitor the reaction. Runs were performed under zero-order conditions with indan-1-one concentrations *ca.* 1 × 10^{-3} mol dm^{-3}, stoichiometric bromine concentrations *ca.* 1 × 10^{-4} mol dm^{-3}, and bromide ion concentration 0.10 mol dm^{-3}. Bromide ion was supplied either as HBr, to provide variable acidity, or as NaBr to maintain the ionic strength at 0.10 mol dm^{-3}. Absorbance measurements were made using a Cary Model 2200 spectrometer, whose cell compartment was thermostatted at 25 ± 0.05 °C.

In a typical experiment, aqueous hydrobromic acid solution (3.0 cm^3) and dilute aqueous bromine solution (5 µl) were added to a cuvette and this was brought to temperature equilibrium with the spectrometer cell compartment. An acetonitrile solution of indan-1-one (5 µl) was then added to the cuvette to initiate the reaction. The disappearance of Br_3^- was followed for *ca.* 1% consumption of indan-1-one, over which range it was accurately zero-order. Observed first-order rate constants were calculated from zero-order rates of decrease in absorbance, $-dA/dt$, using eqn. (1) with ε_{320} = 5515 dm^3 mol^{-1} cm^{-1} [8] and

$$k_{obs}/s^{-1} = (-dA/dt)\{1 + 1/(K_{ass}[Br^-])\}/(\varepsilon_{320}[\text{indan-1-one}]) \quad (1)$$

K_{ass} (the $Br_2 + Br^-$ association constant) = 16.7 dm^3 mol^{-1}.[9] The observed change in absorbance of Br_3^- for a run followed to completion, in 3.0 mol dm^{-3} perchloric acid solution, indicated that the enolization reaction has a bromine : ketone stoichiometry of 1 : 1.

Rates of acid-catalysed enolization of indan-1-one were also measured by iodine scavenging of the enol in the presence of iodide ion (0.01 mol dm^{-3}) monitoring the absorbance of I_3^-, at λ = 351 nm. Zero-order rates were obtained in aqueous $HClO_4$ with a 500-fold excess of ketone over I_2. Solutions containing $HClO_4$, I_2, NaI and $NaClO_4$ (to keep the ionic strength constant at 0.1 mol dm^{-3}) were first allowed to come to temperature equilibrium with the cell compartment of the spectrometer; reactions were then initiated by adding a known volume of indan-1-one. First-order rate constants were calculated from zero-order rates using eqn. (2). In eqn. (2), ε_{351}

$$k_{obs}/s^{-1} = (-dA/dt)\{1 + (K/[I^-])\}/(\varepsilon_{351}[\text{indan-1-one}]) \quad (2)$$

is the molar extinction coefficient of I_3^- at λ = 351 nm, ε_{351} = 26 000 dm^3 mol^{-1} cm^{-1}, and K is the equilibrium constant for the $I_3^- \longrightarrow I_2 + I^-$ reaction ($K = 1.5 \times 10^{-3}$ mol dm^{-3}).[10]

Results

Reaction identification

HPLC analysis of an aqueous solution of 2-methoxyindan-1-one (10^{-4} mol dm^{-3}), which had been subjected to one flash-photolysis pulse, revealed only one photolysis product (60%), in addition to unchanged starting material (40%).† Spiking the solution with an authentic sample identified the photolysis product as indan-1-one. These observations indicate that flash photolysis of 2-methoxyindan-1-one, in aqueous solution, results in the clean formation of indan-1-one.‡ Evidence for 3-hydroxyindene, an intermediate, comes from flash photolysis of a D_2O solution of 2-methoxyindan-1-one, which showed incorporation of one deuterium atom into indan-1-one, according to mass spectrometric analysis. The presence of formaldehyde in the photolysate was established by the use of the Hantzsch reaction which generates 3,5-diacetyl-1,4-dihydrolutidine (λ_{max} = 410 nm) from formaldehyde, ammonia and acetylacetone.[11]

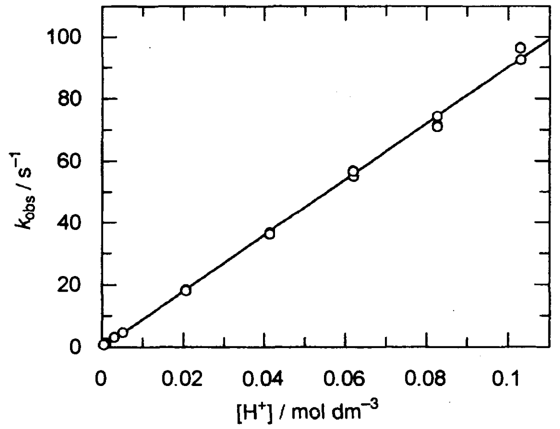


Fig. 1 Relationship between perchloric acid concentration and rates of ketonization of 3-hydroxyindene in aqueous solution at 25 °C

Ketonization of 3-hydroxyindene in aqueous acid

Rates of ketonization of 3-hydroxyindene, generated by the flash photolysis of 2-methoxyindan-1-one, were measured in aqueous perchloric acid solution by monitoring the increase in ketone absorbance at λ = 295 nm. Observed first-order rate constants were determined over the concentration range $[HClO_4]$ = 0.0005–0.1 mol dm^{-3}. The data are summarized in Table S1 § and displayed in Fig. 1. As this figure shows, the observed rate constants are accurately proportional to acid concentration; least-squares analysis provides the hydronium ion catalytic coefficient, $k_{H^+}{}^K$ = (904 ± 8) dm^3 mol^{-1} s^{-1}, determined at ionic strength = 0.1 mol dm^{-3}. This value is in good agreement with a previous estimate for ionic strength = 1.0, $k_{H^+}{}^K$ = 903 dm^3 mol^{-1} s^{-1}, obtained by extrapolation of ketonization rates determined in acetonitrile–water mixtures.[12]

The rate constant for the ketonization of 3-hydroxyindene is 16 times larger than that for the hydronium ion catalysed hydrolysis of 3-methoxyindene (k_{H^+} = 58 dm^3 mol^{-1} s^{-1})[13] which is consistent with the *ca.* 20-fold greater reactivity usually found for enols compared with the corresponding methyl vinyl ethers.[1]

Rates of ketonization of indan-1-one enol were measured in D_2O solutions of perchloric acid over the concentration range 0.02–0.10 mol dm^{-3}; the data are summarized in Table S2. Least-squares analysis provides the catalytic coefficient $k_{D^+}{}^K$ = (244 ± 4) dm^3 mol^{-1} s^{-1}. Combination of this result with the value obtained in H_2O gives the isotope effect, k_{H^+}/k_{D^+} = 3.70 ± 0.07. This solvent isotope effect is in the normal direction and of the magnitude expected for rate-determining proton transfer from the hydronium ion to carbon, which is the mechanism by which enols are known to undergo ketonization (Scheme 3).[1]

Enolization of indan-1-one in aqueous acid

The acid-catalysed halogenation of a ketone such as indan-1-one in aqueous solution is known to occur in two stages:

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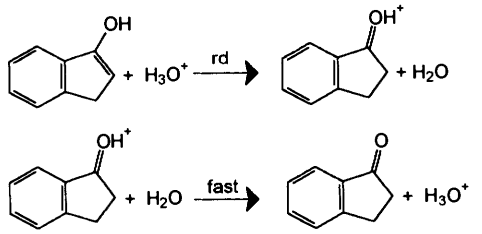
† These percentages were obtained using extinction coefficients of the compounds at the UV detector wavelength (λ = 254 nm).

‡ Steady-state photolysis of ethanolic solutions of 2-methoxyindan-1-one gives indan-1-one (70%) and a cyclic product (30%), resulting from cyclization of a biradical intermediate.[2c]

§ Supplementary material: Tables S1–S10 of rate data have been deposited with the British Library [Supp. No. 57108 (8 pp.)]. For details of the supplementary publications scheme see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1.



Scheme 3

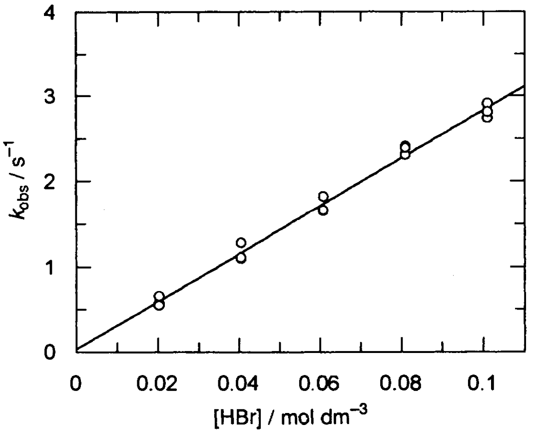
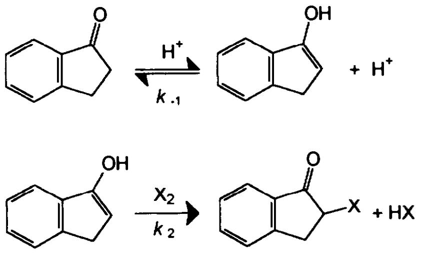


Fig. 2 Relationship between hydrobromic acid concentration and rates of enolization of indan-1-one in aqueous solution at 25 °C

formation of the enol, followed by reaction of this intermediate with halogen (X = Br, I, Scheme 4).[14] Formation of the enol



Scheme 4

will be the rate-determining step, and the rate of halogen consumption will consequently measure the rate of the enolization reaction, when the enol reacts with halogen sufficiently more rapidly than it undergoes acid-catalysed reversion to ketone.

Rates of enolization of indan-1-one were measured in dilute hydrobromic acid solutions, [HBr] = 0.02–0.1 mol dm^{-3}, by using bromine to scavenge the enol and observed first-order rate constants were calculated from zero-order rates. The data are summarized in Table S3 and displayed in Fig. 2. It can be seen that these rate constants are accurately proportional to acid concentration; least-squares analysis provides $k_{\mathrm{H}^+}^{\mathrm{E}} = (2.80 \pm 0.07) \times 10^{-5}$ dm^3 mol^{-1} s^{-1}. Rates of enolization were also measured in dilute perchloric acid solutions, [HClO$_4$] = 0.06–0.02 mol dm^{-3}, using iodine to scavenge the enol; observed first-order rate constants were calculated from zero-order rates and these data are summarized in Table S4. The rate constants are accurately proportional to acid concentration and least-squares analysis gives $k_{\mathrm{H}'}^{\mathrm{E}} = (3.1 \pm 0.1) \times 10^{-5}$ dm^3 mol^{-1} s^{-1}. These two estimates for $k_{\mathrm{H}'}^{\mathrm{F}}$ are in agreement and average to $k_{\mathrm{H}^+}^{\mathrm{E}} = (2.95 \pm 0.09) \times 10^{-5}$ dm^3 mol^{-1} s^{-1}. This second-order rate constant for the enolization of indan-1-one, determined at ionic strength = 0.10 mol dm^{-3}, is higher than a previously reported value for ionic strength = 1.00 mol dm^{-3}, $k_{\mathrm{H}^+}^{\mathrm{E}} = 1.67 \times 10^{-5}$ dm^3 mol^{-1} s^{-1}.[12]

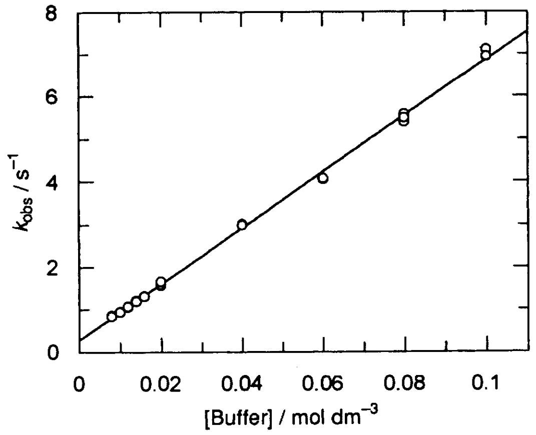


Fig. 3 Relationship between buffer concentration and observed first-order rate constants for the ketonization of 3-hydroxyindene in aqueous acetic acid buffer solutions ([HOAc]/[OAc] = 1)

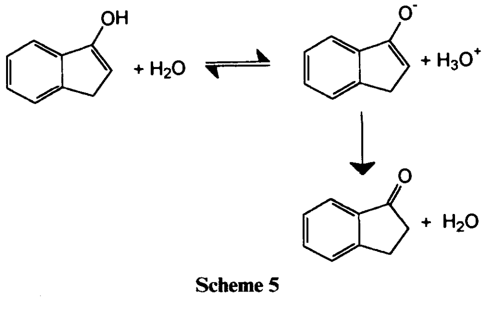
Ketonization in acetic acid buffers

Rate measurements were made in a series of buffer solutions of constant ionic strength (0.10 mol dm^{-3}) and constant buffer ratio, but changing buffer concentration (five-fold variation). Three series were used with [HOAc]/[OAc] = 3, 1 and 1/4, and rates of ketonization were measured by monitoring the increase in ketone absorbance at λ = 295 nm. With the series of buffer ratio = 3, buffer failure occurred and hydronium ion concentrations dropped at low buffer concentration.[15] Observed rate constants were therefore adjusted to a common hydronium ion concentration using the known hydronium ion catalytic coefficient determined in perchloric acid solutions; hydronium ion concentrations needed for this purpose were obtained by calculations using literature pK_a values and activity coefficients recommended by Bates.[16] The rate data are summarized in Table S5.

Observed rate constants within each buffer series proved to be accurately proportional to buffer concentration and the data were fitted to the rate law of eqn. (3) by linear least-squares

$$k_{\mathrm{obs}}(\text{or } k_{\mathrm{adj}}) = k_x^{\mathrm{K}} + k_{\mathrm{cat}}^{\mathrm{K}}[\text{buffer}] \qquad (3)$$

analysis; Fig. 3 shows a typical example. The extrapolated values of k_x^{K} proved to be constant, k_x^{K} (average) = (0.26 ± 0.04) s^{-1}, over the hydronium ion concentration range employed, (8.14–0.68) × 10^{-5} mol dm^{-3}. This represents a hydronium ion concentration region where ketonization takes place by an 'uncatalysed' mechanism; a solvent water molecule acts as a basic proton acceptor and this is then followed by carbon protonation with the hydronium ion thus formed (Scheme 5).



Scheme 5

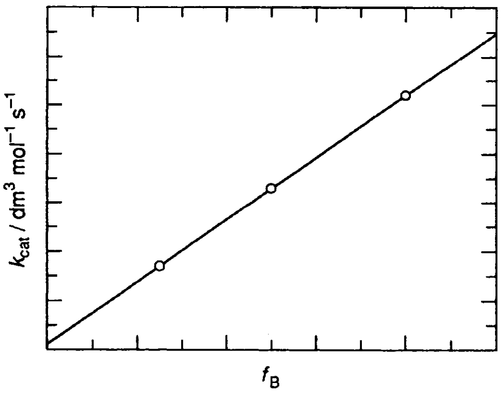


Fig. 4 Relationship between buffer catalytic coefficients and fraction of buffer present in the basic form for the ketonization of 3-hydroxyindene in acetic acid buffer solutions

The catalytic coefficients, k_{cat}, obtained by eqn. (3) were partitioned into reaction through the acidic and basic components of the buffer, according to eqn. (4), in which k_{HA} and k_B

$$k_{cat} = k_{HA} + (k_B - k_{HA})f_B \qquad (4)$$

are the general-acid and general-base catalytic coefficients, respectively, and f_B is the fraction of buffer present in the basic form.

Fig. 4 illustrates the application of this method to the ketonization of 3-hydroxyindene in acetic acid buffers, using the data located in Table S6. Least-squares fitting gave the results $k_{HA} = 2.3 \pm 0.2$ dm^3 mol^{-1} s^{-1} and $k_B = 127.3 \pm 0.4$ dm^3 mol^{-1} s^{-1}, which shows that buffer catalysis is mainly of the general-base type with only a small contribution from general-acid catalysis.

Ketonization in ammonia buffers and sodium hydroxide solutions

Rate measurements were made in a series of ammonia buffers of varying buffer concentration but constant buffer ratio, which, at the constant ionic strength employed, served to hold hydrogen ion concentrations constant along a buffer series. Seven buffer series were used with $[NH_4^+]/[NH_3] = 0.20, 0.38, 0.70, 1.03, 2.00, 3.00$ and 5.00. The decrease in absorbance of either the enol ($\lambda = 267$ nm) or the enolate ion ($\lambda = 290$ nm) was monitored. Observed first-order rate constants proved to be accurately proportional to buffer concentration in a given buffer series, and buffer-independent rate constants, k_x^K, were obtained by least-squares fitting of eqn. (3). Rates of ketonization of 3-hydroxyindene were also measured in dilute aqueous sodium hydroxide solutions, [NaOH] = 0.10–0.0050 mol dm^{-3}. The buffer-independent rate constants, together with the observed rate constants determined in sodium hydroxide solution, are located in Tables S7 and S8, respectively, and are plotted in Fig. 5. The rate constants increased with decreasing hydronium ion concentration (base catalysis) eventually reaching a constant maximum value (base catalysis saturation). This behaviour is expected for enol ketonization; it represents a shift in initial state from enol at low basicity to the more reactive enolate ion at high basicity. Base-catalysis saturation occurs when the equilibrium shown in Scheme 6 shifts completely from enol to enolate. The rate law that applies to ketonization of an enol in basic solution is shown in eqn. (5), in which k_o' is the rate

$$k_{obs}/\mathrm{s}^{-1} = k_o' K_a^E / (K_a^E + [H^+]) \qquad (5)$$

constant for carbon protonation of the enolate by water and K_a^E is the acidity constant of the enol. Least-squares analysis using

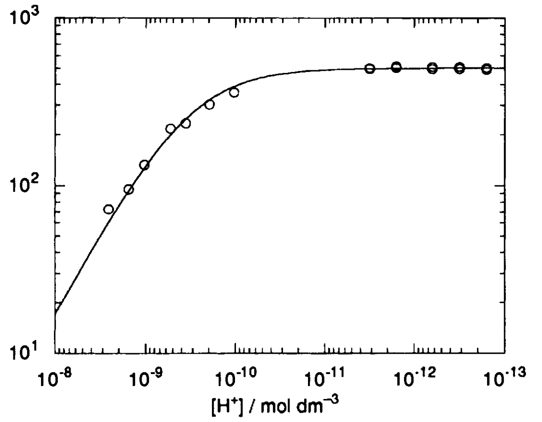
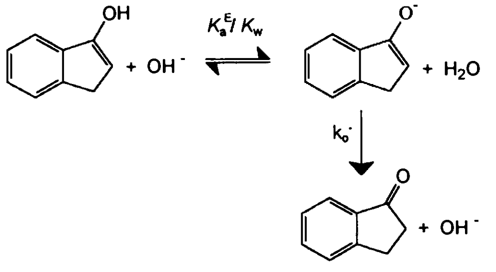


Fig. 5 Ketonization of 3-hydroxyindene in aqueous solution at 25 °C

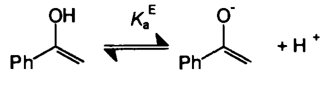


Scheme 6

eqn. (5) gives $k_o' = 501 \pm 3$ s^{-1} and $K_a^E = (3.3 \pm 0.2) \times 10^{-10}$, p$K_a^E = 9.48 \pm 0.02$.

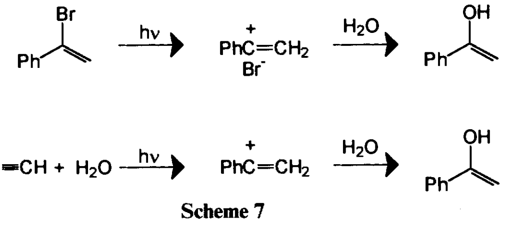
Determination of the pK_a^E of acetophenone enol

The pK_a^E of acetophenone enol, eqn. (6), was determined



(6)

kinetically by construction of its rate profile for ketonization both at and near the region of base catalysis saturation. Acetophenone enol was generated by flash photolysis of solutions of either α-bromostyrene (photosolvolysis)[6d] or phenylacetylene (photohydration),[6a,d] according to Scheme 7.



Scheme 7

The rates of ketonization of acetophenone enol were measured in a series of five ammonia buffer solutions, buffer ratio = 5, 3, 1, 0.4 and 0.2, with varying buffer concentration. The decay of the enol was monitored at $\lambda = 270$ nm and buffer-independent rate constants were obtained by least-squares fitting of the rate data within a buffer series, using eqn. (3). Rates of ketonization of acetophenone enol were also measured in [NaOH] solutions (0.000 50–0.10 mol dm^{-3}) by determining the decrease in the enolate absorbance at $\lambda = 287$ nm. The buffer-independent rate constants, together with the observed rate constants determined in sodium hydroxide solutions were analysed using eqn. (5) to give $k_o' = (8.6 \pm 0.2) \times 10^3$ and

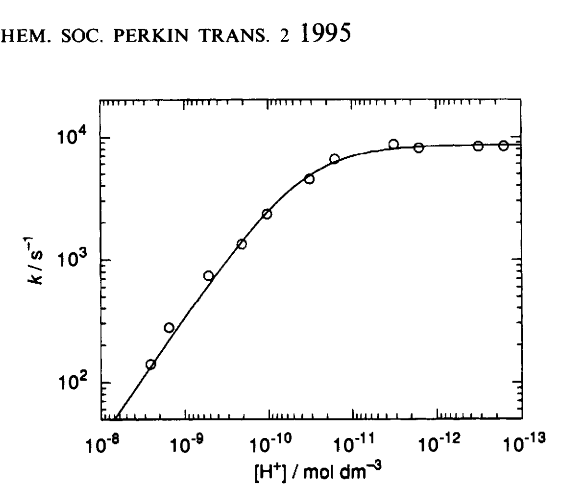


Fig. 6 Ketonization of 1-acetophenone enol in aqueous solution at 25 °C

Table 1 Comparison of indan-1-one and acetophenone keto–enol systems[a]

Parameter	Indan-1-one	Acetophenone[b]
pK_E	7.48	7.96
pK_a^E	9.48	10.40[c]
pK_a^K	16.96	18.31
$k_{H^+}^E/10^{-5}$ dm^3 mol^{-1} s^{-1}	2.95	1.21
$k_{H^+}^K/10^3$ dm^3 mol^{-1} s^{-1}	0.904	1.25

[a] Ionic strength = 0.1 mol dm^{-3}; equilibrium constants are concentration quotients at this ionic strength. [b] Ref. 3(*a*) and 9. [c] Determined in this work.

$K_a^E = (4.0 \pm 0.4) \times 10^{-11}$; $pK_a^E = (10.40 \pm 0.04)$. The data are located in Table S9 and S10 are displayed in Fig. 6. The pK_a^E value determined here agrees nicely with that obtained by a spectrophotometric titration curve ($pK_a^E = 10.34 \pm 0.05$).[3b]

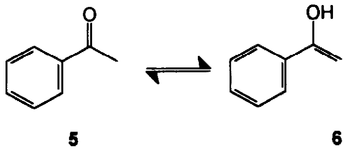
Discussion

Keto–enol equilibrium constant

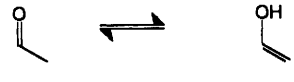
It is often difficult to determine the keto–enol equilibrium constant of a simple enol, such as 3-hydroxyindene, by direct measurement of the equilibrium concentration of enol because this concentration is usually very small. However, in such a situation, an equilibrium constant can be obtained by taking the ratio of the rate constants for reaction in both the forward (enolization) and reverse (ketonization) directions. The hydronium-ion catalytic coefficients determined here for the ketonization of 3-hydroxyindene and the enolization of indan-1-one can be used in this way to determine the keto–enol equilbrium constant for this system: $K_E = k_{H^+}^E/k_{H^+}^K = (3.3 \pm 0.1) \times 10^{-8}$, $pK_E = 7.48 \pm 0.01$. This keto–enol equilibrium constant, determined at ionic strength = 0.1 mol dm^{-3}, is 1.8 times greater than a previous estimate for ionic strength = 1.0 mol dm^{-3}, $K_E = 1.85 \times 10^{-8}$.[12]

α-Phenyl substitution is known to decrease enol content; this is evident, for example, in a comparison of the keto–enol equilibrium constant of acetophenone (**5**), $pK_E = 7.96$,[9] with that of acetaldehyde, (**7**), $pK_E = 6.23$.[5b] A phenyl substituent is known to stabilize double bonds by conjugation; Hine's double-bond stabilizing parameter for phenyl is $D = 4.9$ kcal mol^{-1}.[17] α-Phenyl substitution is stabilizing towards both the keto and enol forms of acetophenone compared with an α-hydrogen substituent. Initial-state stabilization of keto form **5** by phenyl is more important than phenyl stabilization in **6** since acetophenone has a lower enol content than acetaldehyde.

What is the effect of a fused *versus* an unfused phenyl substituent on an enol–keto equilibrium? In 3-hydroxyindene coplanarity is forced upon the system through the presence of a small ring. As shown in Table 1, indan-1-one has a lower pK_E than acetophenone ($\Delta pK_E \approx 0.5$). At first, this result appears contradictory since the enforced coplanarity of the phenyl system in indan-1-one should increase the phenyl effect on the pK_E, which results in lowering of the enol content. However, indan-1-one enol is β-alkyl-substituted unlike acetophenone enol, and this effect increases enol content. This is evident in 2,2-dimethylacetophenone ($pK_E = 6.48$) having a lower enol content than acetophenone ($pK_E = 7.96$).[18] The β-alkyl substitution in indan-1-one enol then masks the planar phenyl effect on the keto–enol equilibrium constant of indan-1-one.



5 **6**



7 **8**

Enol acidity constant

There is usually not much variation in pK_a^E values of simple enols; acetophenone enol ($pK_a^E = 10.40 \pm 0.04$) is a stronger oxygen acid compared with acetaldehyde enol ($pK_a^E = 10.50 \pm 0.02$)[5b] by *ca.* only 0.1 p*K* unit. However, 3-hydroxyindene ($pK_a^E = 9.48 \pm 0.02$) is found to be a stronger oxygen acid than acetophenone enol ($pK_a^E = 10.40 \pm 0.04$) by *ca.* 1 p*K* unit ($\delta\Delta G = 1.3$ kcal mol^{-1}). An α-phenyl substituent can stabilize the enolate relative to the enol by an electron-withdrawing polar effect. There should, however, be little difference in polar effect between the planar 3-hydroxyindene and the non-planar acetophenone enol systems, and the greater acidity of 3-hydroxyindene then implies that some other effect must be operating. Although no formal resonance structure can be drawn delocalizing negative charge from the enolate ion into the benzene ring of these systems, the fact that the highest occupied molecular orbital of the enolate ion has a non-zero coefficient on the central carbon atom[19] suggests that such an interaction is possible. This stabilizing interaction will be stronger in the planar than in the non-planar system, and that will make 3-hydroxyindene a stronger acid than acetophenone enol.

Ketone acidity constant

The enolization reaction of indan-1-one and the ionization of 3-hydroxyindene as an oxygen acid form two legs of a thermodynamic cycle whose third member is the ionization of indan-1-one as a carbon acid, Scheme 2. The equilibrium constant for this carbon acid ionization, K_a^K, can be found as the product of the equilibrium constants for the other two reactions: $K_a^K = K_E K_a^E = (1.09 \pm 0.07) \times 10^{-17}$, $pK_a^K = 16.96 \pm 0.03$.

A comparison of the carbon acidities of indan-1-one and acetophenone reveals a 1.4 p*K* unit difference for the acidifying effect of a fused (enforced coplanarity) *versus* an unfused phenyl substituent. The difference here arises mainly from the greater acidity of indan-1-one enol compared with acetophenone enol. Differences in pK_a usually parallel differences in the keto–enol equilibrium constant,[1] but in this case the enol acidity constant has a larger influence on the keto acidity constant.

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