Detritiation Kinetics of Acetophenones in Highly Acidic Media

By **Derek W. Earls**,† Department of Chemistry, University of Surrey, Guildford GU2 5XH

The detritiation kinetics and equilibrium protonation characteristics of a series of ring substituted acetophenones have been studied at 50 °C in highly acidic media comprising aqueous sulphuric acid. The rates of detritiation of the acetophenones pass through a maximum in the region of wt. % H_2SO_4 at which they are half-protonated. Of the various mechanistic criteria available the Bunnett–Olsen ϕ value treatment proves the only reliable one. This treatment also holds well for the determined kinetic data on the detritiation of acetophenone in concentrated hydrochloric acid.

SINCE the 1930's a variety of theoretical and semi-empirical approaches have been developed for predicting or testing reaction mechanisms based on the observed rates of reactions in concentrated aqueous acid solutions. These approaches comprise the 'Zucker–Hammett hypothesis'[1] now largely discredited, the Bunnett w and w^* treatments,[2,3] the Bunnett and Olsen ϕ values treatment,[3–5] and the Kresge α coefficient treatment.[6] Rochester[7] has given a comprehensive summary of experimental kinetics in highly acidic media and the success, or otherwise, of the various mechanistic criteria. He has also reviewed the work on acidity functions in high acidic media. Early work[8,9] on the halogenation of ketones led to the now well authenticated[10] mechanism for the acid-catalysed enolisation reaction. Hammett and Zucker[11] studied the acid-catalysed iodination of acetophenone in $HClO_4$ and H_2SO_4, the results in $HClO_4$ being used, in part, in the deductions of the 'Zucker–Hammett hypothesis'. The rates in H_2SO_4 were studied up to 66 wt. % H_2SO_4; however, reaction of the enol with iodine became rate limiting above 51 wt. % H_2SO_4. Bunnett[3,4] later used the results for the reactions as standards in his w, w^*, and ϕ value mechanistic criteria treatments. The halogenation of acetone in aqueous HCl has also been studied.[12,13] Deductions in terms of the 'Zucker–Hammett hypothesis'[13] are complicated by the uncertainty in the value of pK_{SH^+} for acetone.[14] Nevertheless, the w and w^* values for the reaction are consistent with water acting as a proton transfer agent in the rate-determining step. Work by Baliga and Whalley[15] on the effect of pressure on the acid-catalysed enolisation of acetone and acetophenone in various ethanol–water solvents also supports the accepted mechanism. Swain and Rosenberg[16] have studied the isomerisation of D-α-phenylisocaprophenone in 85—94 wt. % H_2SO_4. They fitted the data to an empirical expression for the rate constant that accounted for the amount of protonated form of the substrate and for catalysis by both water and hydrogen sulphate ion. However, Long and Bakule[17] criticised the treatment since concentrations rather than activities of the catalytically active species were used. They found that the interconversion of the keto and enol forms of cyclohexane-1,2-dione correlated better with H_0 than with the catalyst acid concentration. This observation and the observed w and w^* values for the forward and reverse reactions were explained in terms of the accepted mechanism with the additional proposal that the transition state for the reaction contains an extra molecule of water for the reaction studied. The ϕ value for the reaction implies that the contradiction between Hammett–Zucker and Bunnett treatments arises because of differential medium effects on the keto and enol forms in concentrated acid solution. Noyce and his

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† *Present address:* Countess Weir Laboratory, South West Water Authority, Exeter, Devon.

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co-workers[18] have made detailed studies of the acid-catalysed isomerisation of *cis*-chalcones. Depending on the substituents present in the chalcones, correlation of the rates with H_0 may or may not be obtained. This observation and the variation of the Bunnett w values with the substituent present is explained in terms of two competing mechanisms, *viz.* fast oxygen protonation followed either by slow attachment of water to the β-carbon of the carbon–carbon double bond, or by slow unimolecular rotation about the carbon–carbon double bond.

Although a great deal of kinetic work for reactions in highly acidic media has been reported, there is a comparative scarcity of data over large ranges of acidity,[19] particularly up to 17—18M-H_2SO_4. This implies a lack of truly rigorous testing of the various criteria for mechanism in high acidic media. In particular the acid-catalysed enolisation of ketones has not been investigated above 9M-acid. Furthermore, for many of the reactions studied, no data was available on the protonation equilibria, in highly acidic media, for the compounds under study. Clearly kinetic data for a reaction with an established mechanism, followed over a large range of acidity, coupled with a knowledge of the protonation characteristics of the compound or compounds under study, would provide a valuable test of the existing mechanistic criteria for reactions in highly acidic media.

EXPERIMENTAL

The acetophenones were obtained commercially, solids being purified by recrystallisation from ethanol–water and liquids by distillation under reduced pressure. M.p.s. and b.p.s. of the purified acetophenones were in good agreement with reported values.[20] AristaR grade sulphuric acid was diluted with doubly deionized freshly boiled-out water to produce solutions of varying wt. % H_2SO_4. Laboratory grade fuming sulphuric acid was used to produce solutions containing excess of sulphur trioxide in the protonation equilibrium measurements. Solutions were made up by weight and were checked by titration of the accurately diluted solution against sodium hydroxide solution standardised with potassium hydrogen phthalate. Laboratory grade trimethylammonium chloride was used from a 50 wt. % aqueous solution. AnalaR grade hydrochloric acid (d = 1.16) was diluted with doubly deionized, freshly boiled-out water to produce solutions of varying concentration of hydrochloric acid, molarities being determined by titration. The acetophenones were tritiated by reacting for 24 h at room temperature 1 g of the compound, 0.05 ml tritiated water (specific activity 200 mCi ml^{-1}), 1 pellet of sodium hydroxide, and sufficient AnalaR dioxan to make the mixture, above the excess of sodium hydroxide, homogeneous. The tritiated compound was separated out by addition of excess of water and filtration (or extraction with ether for the liquids).

The equilibrium protonation characteristics of the acetophenones were determined by a ^{1}H n.m.r. method described by Haake and his co-workers,[21] the n.m.r. spectra of sulphuric acid solutions, 0.1M in acetophenone and tetramethylammonium ion, being measured on a Perkin-Elmer R10 60 MHz spectrometer operating with a variable temperature probe maintained at 50 ± 0.3 °C. The spectra were run at least three times and the average chemical shift from the internal standard obtained, the chemical shifts being measured between the tips of the sharp peaks produced. Shifts were always reproducible to ±0.01 p.p.m. The results are summarised in Table 1. The values of d_S and d_{SH^+} for the non-ideal sigmoid curves produced (chemical shift d *versus* H_0) are determined as suggested by Lee[22] thus minimising errors due to the non-ideal curves.[23,24] The indicator ratio (I) is given by equation (1).

TABLE 1

Chemical shift data for the protonation of some acetophenones in sulphuric acid solutions at 50 °C: 1, acetophenone; 2, *p*-bromoacetophenone; 3, *p*-nitroacetophenone; 4, *p*-dimethylaminoacetophenone; 5, *p*-methoxyacetophenone

	Chemical shifts (p.p.m. × 10)				
Wt. % H_2SO_4	1	2	3	4	5
34.1	−2.85		−2.30	−2.56	−3.26
39.4	2.85		2.20	2.55	3.25
44.0	2.85	−3.00	2.20	2.38	3.20
48.5	2.90	3.00	2.20	2.42	3.10
53.7	2.75	2.92	2.18	2.34	2.92
55.8	2.77	2.75		2.40	2.83
58.3	2.64	2.85	2.10	2.25	2.23
60.5	2.66	2.58	2.12	2.26	1.61
63.2	2.38	2.47	2.13	2.16	1.13
65.8	2.18	2.20	2.00	2.05	0.90
68.4	1.47	2.00	1.90	1.91	−0.20
70.7	1.15	1.53	1.61	1.77	+0.05
73.1	−0.23	−0.40	1.40	1.56	0.40
75.7	+0.58	+0.28	1.30	1.17	0.59
78.2	1.20	1.00	0.90	0.82	0.75
80.5	1.70	1.35	−0.55	−0.20	0.73
82.6	2.16	1.70	0.00	+0.29	0.79
85.1	2.36	1.95	+0.69	1.05	0.75
87.4	2.40	2.05	1.43	1.83	0.78
89.7	2.50	+2.10	2.13	2.33	0.78
92.5	2.57		2.80	3.13	0.78
95.5			3.50	3.50	
96.0	+2.73		3.65	3.60	+0.78
98.3			3.80	3.73	
98.4			3.90	3.75	
98.7			3.90	3.80	
99.8			4.40	4.10	
100.4			4.65	4.20	
100.9			+4.65	+4.20	
d_S	−2.85	−3.10	−2.20	−2.40	−3.28
d_{SH^+}	+2.85	+2.30	+4.80	+4.60	+0.78

$$I = C_{SH^+}/C_S = (d - d_S)/(d_{SH^+} - d) \qquad (1)$$

In the kinetic runs which involved following the decrease in activity of the tritiated substrate the technique used is essentially that described by Jones.[25] In some kinetic runs in hydrochloric acid the increase in tritium content of the aqueous portion of the reaction mixture was followed by techniques reported earlier.[26] The reproducibility of rate

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TABLE 2

Summary of kinetic data in sulphuric acid at 50° $10^5k^T/s^{-1}$

Wt. % H_2SO_4	Acetophenone	p-NO_2-acetophenone	p-MeO-acetophenone	p-Br-acetophenone	p-$(CH_3)_2N$-acetophenone
39.4	10.8	5.63			
40.4			12.1	10.9	6.76
45.6	17.7	9.09			
47.5			18.4	17.4	12.0
52.0	26.3	16.3	21.7	23.3	16.2
57.3	36.9	25.4	24.1	32.9	25.0
63.5	54.0	41.5			
64.0			19.5	51.9	43.1
68.9			11.6	65.4	66.2
69.2	60.5	73.5			
77.8	28.8	155	2.12	46.4	129
87.2	3.58	204		6.78	116
99.1		50.7			19.2

constants was ±2%. To check that no side reaction occurred during the course of a run, the u.v. spectra of the acetophenone solutions were monitored. No changes were observed with time except for p-methoxyacetophenone above 85 wt. % H_2SO_4. Table 2 gives the results in aqueous H_2SO_4 and Table 3 the results for acetophenone in aqueous HCl.

TABLE 3

Observed rate constants for the detritiation of acetophenone in HCl solutions at 50°

HCl/M	$10^5k^T/s^{-1}$	Kinetic method
0.311	0.132	*c*
1.15	0.573	*a*
2.20	1.26	*a*
3.06	2.10	*a*
4.19	3.74	*c*
	3.85	*b*
	3.84	*a*
5.58	7.43	*a*
5.95	8.63	*a*
6.10	9.20	*a*
	9.03	*a*
	8.98	*b*
6.96	13.6	*a*
	13.4	*a*
7.15	14.2	*a*
7.95	21.3	*a*
8.93	31.6	
9.94	49.3	*a*

[a] Following the decrease in the tritium content of the tritiated substrate over at least 60% of the total reaction. [b] Following the increase in the tritium content of aqueous portion of the reaction solution over at least 60% of the total reaction. [c] As *b* but using the initial rate method, following <3% of the total reaction.

DISCUSSION

In the absence of unaccounted for solvent effects on the observed n.m.r. spectra, pK_{SH^+} is given by equation (2).

$$\log_{10}I = -mH_x + pK_{SH^+} \qquad (2)$$

The results using the H_0,[27] H_A,[28] and H_B [29] acidity functions are summarised in Table 4. The unexpectedly high region of acidity through which p-dimethylaminoacetophenone protonates is rationalised if the dimethylamino-group is substantially protonated over the range studied. This is borne out by the kinetic results discussed later. Examination of Table 4 shows that the values of pK_{SH^+} derived from mH_x show considerable scatter for each acetophenone and, moreover, the relative values for the various acetophenones are not in any logical order. The protonation of the acetophenones does, however, follow the H_B scale more closely than the H_0 or H_A scales. It is evident that the view that weak base pK_{SH^+} values are still not even operationally defined [30] is given considerable support by the results.

TABLE 4

Summary of protonation equilibria results: wt. % H_2SO_4 values refer to the half-protonation point

p-Methoxyacetophenone wt. % H_2SO_4 = 62.6

m values	H_0 0.78	mH_x values	H_0 −3.7
	H_A 1.5	at half-protonation	H_A −4.8
	H_B 1.1		H_B −5.1

p-Bromoacetophenone wt. % H_2SO_4 = 76.2

m values	H_0 0.58	mH_x values	H_0 −3.9
	H_A 1.2	at half-protonation	H_B −5.1
	H_B 1.0		H_A −6.0

Acetophenone wt. % H_2SO_4 = 74.0

m values	H_0 0.63	mH_x values	H_0 −4.0
	H_A 1.2	at half-protonation	H_A −4.8
	H_B 1.0		H_B −5.8

p-Dimethylaminoacetophenone wt. % H_2SO_4 = 85.9

m values	H_0 0.45	mH_x values	H_0 −3.7
	H_B 0.76	at half-protonation	H_B −5.3

p-Nitroacetophenone wt. % H_2SO_4 = 86.6

m values	H_0 0.45	mH_x values	H_0 −3.8
	H_B 0.75	at half-protonation	H_B −5.2

Examination of Table 2 reveals that the rates of detritiation of the acetophenones pass through a maximum in the region of wt. % H_2SO_4 at which they are half-protonated (Table 4). Such behaviour has been observed for other reactions in concentrated H_2SO_4, *e.g.* in the decarboxylation of aromatic aldehydes,[31] and the hydrolysis of esters,[32] amides,[33] and acetanilides.[34] Moreover, the kinetics of the Schmidt reaction with substituted acetophenones in aqueous H_2SO_4 has been studied by Tereshchenko *et al.*[35] and the dependence of the rate

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constant of the second-order reaction on H_0 has the form of a curve with a maximum which is discussed in terms of the acid–base equilibrium of the initial reactants.

The present results may be qualitatively explained in terms of rate enhancement due to substantial protonation of the acetophenones followed by rate decrease due to a decrease in the activity of water with increasing wt. % H_2SO_4. Quantitative treatment of the results in terms of the various mechanistic criteria mentioned earlier is more difficult. From the results in Table 4 it is clear that treatments requiring a knowledge of accurate pK_{SH^+} values present problems. However, scrutiny of the treatments due to Bunnett (*w* and *w**) and Bunnett–Olsen (ϕ) indicates a requirement of a K_{SH^+} parameter which reflects the half-protonation value of h_0 for the compounds under study, since it is in the region where $K_{SH^+} \simeq h_0$ that kinetic maxima are expected for reactions proceeding *via* the *A*-2 mechanism. In the light of this, the present results have been subjected to the various mechanistic treatments using values of h_0 on the Jorgenson and Hartter scale and using a value of h_0 corresponding to half-protonation for the value of K_{SH^+}. While it is accepted that this is not strictly correct it is certainly more meaningful, in the light of the original semi-empirical nature of the various treatments than using the particularly low pK_{SH^+} values given in Table 4. Even a cursory examination of the various mechanistic criteria shows that the treatments break down when using these lower values of pK_{SH^+}. Table 5 summarises all the results. The values of concentration of H^+, C_{H^+} used in the Bunnett–Olsen ϕ value treatment are taken from reported Raman data.[36] The values for the activity of water (a_w) used in the Bunnett *w* and *w** treatments are reported values [37] which are available only at 25 °C. The Bunnett *w* and *w** treatments are unsatisfactory in that curved plots are obtained. Moreover, the average *w* slopes are outside the empirical limit of >3.3 set by Bunnett for reactions in which water behaves as a proton transfer agent. The curvature may in part be due to the use of a_w values at 25 °C (although Bunnett [38] concludes that the effect of temperature on *w* and *w** is small) and in part due to the use of the particular K_{SH^+} value chosen. It has, however, been foreseen [39] that *w* and *w** lines would show curvature when studied over large ranges of acidity and that values of *w* and *w** obtained would be dependent on the particular region of acidity studied.

TABLE 5

Summary of mechanistic criteria treatments

Compound	ω	ω^x	ϕ	α
1	2.2 (c)	−0.5 (c)	0.76 (s)	+0.5 (s)
2	1.7 (c)	−0.5 (c)	0.80 (s)	*ca.* +0.4—0.5 (s)
3	1.7 (c)	−0.6 (c)	0.80 (s)	+0.4 (s)
4	1.7 (c)	−0.6 (c)	0.76 (s)	−ve curve
5	1.6 (c)	−0.7 (c)	0.75 (s)	−ve curve

(c) Curved plots; (s) straight line plots.

1, *p*-Methoxyacetophenone; 2, *p*-bromoacetophenone; 3, acetophenone; 4, *p*-dimethylaminoacetophenone; 5, *p*-nitroacetophenone.

The Bunnett–Olsen ϕ value treatment gives good straight lines for all the compounds studied. Moreover, the values of ϕ are very much in line with those of 0.83 for the iodination of acetone in 0.5—2.2M-HCl, 0.62 for the iodination of acetophenone in 0—6.4M-H_2SO_4 and 0.8 for the iodination of acetophenone in 0—3.6M-$HClO_4$.[3] The consistency of the treatment over such a wide range of acidity is surprisingly good and although the present results depend on the value of K_{SH^+} chosen, it is evident that they are relatively insensitive to the variation in the chosen K_{SH^+}. It should be noted that application of the above treatments using the H_B scale, which the acetophenone protonations follow most closely does not improve the correlation for any of the above mechanistic criteria. The Kresge α-coefficient treatment does not require the use of K_{SH^+} or H_0 values. It does, however, require experimentally observed *I* values. The relevant equation for the *A*-2 mechanism may be derived as follows. The treatment assumes that the activity coefficient of the transition state in the rate-determining step is related to the activity coefficients of the products (f_p) and reactants (f_R) of the step by an expression of the form (3). For the *A*-2 mechanism equation (4) holds.

$$f^{\ddagger} = (\pi f_R)^{1-\alpha}\,(\pi f_p)^{\alpha} \qquad (3)$$

The experimental rate constant k_1 is given by (5) where

$$f^{\ddagger} = (f_{SH^+} f_{H_2O})^{1-\alpha}(f_S f_{H^+})^{\alpha} \qquad (4)$$

k_2 is the rate constant for the rate-determining step.

$$k_1 = \frac{C_S}{C_{S}+C_{SH^+}} \cdot \frac{k_2}{K_{SH^+}} \cdot C_{H^+} \cdot \frac{f_S f_{H^+} a_w}{f^{\ddagger}} \qquad (5)$$

Substitution of expression (4) for $f^{\ddagger}$ into equation (3) and rearrangement of terms gives equation (6) in logarithmic form where C_w is the concentration of water.

$$\log_{10} k_1 \frac{1+I}{IC_w} = \alpha \log_{10} \frac{f_{H_2O} C_{H^+}}{I} + \log_{10} \frac{k_2}{(K_{SH^+})\alpha} \qquad (6)$$

The treatment is, of course, limited to kinetic results in the wt. % H_2SO_4 region where values of the indicator ratio *I* may be accurately measured. Table 5 shows that the treatment breaks down for *p*-nitro- and *p*-dimethylamino-acetophenone giving poorly defined lines of negative slope. This breakdown may in part be due to unaccounted for inherent solvent effects on the n.m.r. spectra used to calculate *I* values.

The treatment of the kinetic data for the detritiation of acetophenone in 0.3—10M-HCl shows that the Bunnett *w* and *w** treatments still exhibit a tendency to curvature towards the *w* and *w** values obtained in H_2SO_4. It should, however, be noted that the values of 3.0 for *w* and −2.4 for *w** for more dilute acid are both outside the limits for a reaction in which water acts as a proton

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transfer agent. This would imply a need for an extension of the limits. The Bunnett–Olsen ϕ value treatment again holds well giving a good straight line of slope 0.57. This value is somewhat lower than those obtained in aqueous H_2SO_4 media where the slope obtained is dependent to some extent on the value of K_{SH^+} chosen and indeed the H_0 scale used.

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