

Kinetics of chlorination of ketones by 1-chlorobenzotriazole

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Abstract. The kinetics of chlorination of aliphatic, aralkyl and alicyclic ketones by 1-chlorobenzotriazole (CBT) have been studied in aqueous acetic acid media. In the presence of a mineral acid (HClO_4), the order of the reaction with respect to [ketone] is one and that with respect to [CBT] is zero, suggesting the enolisation of ketone as the slow step, followed by a fast attack of the halogenating species. A primary kinetic isotope effect ($k_H/k_D = 6.6$) is also noticed, when acetone and acetone- d_6 are used as the substrates. Initial addition of chloride ion leads to a first order dependence on [CBT] and a fractional order (0.6) on [acetone]. Thermodynamic parameters for the reaction have also been reported. A negative Hammett reaction constant ($\rho = -0.57$) has been obtained for the halogenation of substituted acetophenones by CBT.

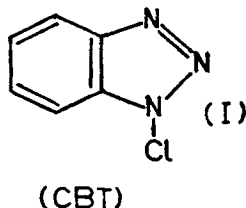
Keywords. 1-Chlorobenzotriazole; chlorination; aliphatic, aralkyl and alicyclic ketones; primary isotope effect; acid catalysis; Hammett reaction constant.

1. Introduction

The halogenation of carbonyl compounds especially the enolisable ones has been the subject of many investigations and the kinetic and synthetic aspects are well documented (de la Mare 1976; Bell 1973). Among the various halogenic electrophiles, molecular halogens have been the most exploited. It has been well established that in acidic media at sufficiently high concentration of halogen, the rate is dependent only on the enolisation of ketone, though there have been instances (Bell and Page 1973; Toullec and Dubois 1973; Bell and Yates 1962) where the generation of a halogenating species turns out to be rate-determining. The prior formation of an adduct (Marshall and Roberts 1971) catalysis by ammonium ions (Bender and Williams 1966) and competing reactions leading to rearrangement (Warnhoff and Teo 1973) are also known to result in complicated kinetic situations. An interesting observation of the rate of chlorination being independent of [ketone] has been reported (Balasubramanian and Thiagarajan 1976) in which the sodium salt of N-chloro toluene-*p*-sulphonamide (Chloramine-T) functions as the halogen source. A study of the halogenation of phenols by the recently developed reagent (Rees and Storr 1968), 1-chlorobenzotriazole

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(CBT) (I) has yielded many interesting results (Srinivasan 1977) and the work we report here comprises of an extension of our kinetic and mechanistic studies with CBT to typical carbonyl systems.



2. Experimental

1-Chlorobenzotriazole was prepared by the method of Rees and Storr from benzotriazole (E Merck sample, melting point 96°C). It was dried and recrystallised (melting point $105\text{--}106^{\circ}\text{C}$) from *n*-hexane.

The liquid organic compounds were purified by distillation from an all-glass apparatus. The solid organic compounds were of extra pure variety. All the inorganic chemicals used were of AR grade. Analar grade acetic acid (BDH) was used after purification by the usual procedure. (Orton and Bradfield 1927).

Solutions of ketone were prepared in aqueous acetic acid mixtures. CBT was dissolved in 100% acetic acid. Both ketone and CBT solutions were thermostated for two hours before each run and they were mixed. 5 ml aliquots of the reaction mixture were pipetted out at regular intervals and quenched in 10 ml of 5% KI solution. 20 ml of 1N H_2SO_4 was added and the liberated iodine was titrated against standard sodium thiosulphate to a starch end point (Berka *et al* 1965).

The reactions were carried under pseudo-molecular conditions. The first order rate constants were evaluated by the numerical method from the integrated rate expression. The zero order rate coefficients were evaluated from a plot of [CBT] against time, the positive slope giving the rate constant. The rate constants were reproducible within $\pm 5\%$. The kinetics were followed nearly to 3 half-lives and reactions were found to be smooth.

3. Product analysis

11.0 g of acetophenone was treated with 1.32 g of CBT in presence of 0.1M HClO_4 and in 50% HOAc–50% H_2O (v/v) medium. When the reaction was complete, acetic acid was neutralised by the addition of solid sodium bicarbonate. The crude crystalline mixture was extracted with chloroform (5×25 ml). It was shaken with dilute hydrochloric acid to remove 1-H benzotriazole. Chloroform was removed by evaporation and the crude compound was recrystallised from alcohol. The product ω -chloroacetophenone has been identified by TLC and by mixed melting point method (m.p. 55°C).

4. Results and discussion

4.1 Chlorination in aqueous acid medium

The chlorination of ketones by CBT proceeds smoothly at 40°C in aqueous acid medium. At low initial concentrations of CBT (3.2×10^{-3} M) the reaction is

found to be zero order in [CBT] (as evidenced by the linearity of a plot of $\{[\text{CBT}]_0 - [\text{CBT}]_t\}$ vs time as also by the constancy of values obtained by the substitution of data in the corresponding rate expression), while it is dependent on the first power of the concentration of ketone (table 1). The order with respect to ketone has been derived from a linear plot of $\log k_0$ vs [ketone], the slope of which is found to be unity.

The reaction is sluggish in the absence of acids. Perchloric and sulphuric acids produce approximately the same catalytic effect, the order with respect to acid in both cases being unity (table 2). The rate law, therefore, is

$$\text{Rate} = k_2 [\text{ketone}] [\text{acid}] \quad (1)$$

Table 1. Effect of concentration of reactants.

[substrate] 10^3 M	[CBT] 10^3 M	$k_0 \times 10^7$ mol $l^{-1}s^{-1}$	$k_1' \times 10^5$ s^{-1}
(a) Acetone			
3.18	4.53	6.51	...
3.18	3.81	6.42	...
3.18	3.20	6.34	1.99
1.91	3.20	3.77	1.97
2.55	3.20	5.07	1.99
5.47	3.20	11.3	2.06
6.88	3.20	14.2	2.06
8.25	3.20	17.6	2.13
9.63	3.20	20.0	2.07
(b) Acetophenone			
5.37	5.39	5.34	...
5.37	2.64	5.19	...
5.37	1.62	4.24	0.79
3.42	1.62	2.60	0.76
2.15	1.62	1.68	0.78
1.79	1.62	1.32	0.74
1.23	1.62	0.91	0.73
(c) Cyclopentanone			
3.47	4.51	16.9	...
3.47	3.96	16.2	...
3.47	3.01	16.6	4.80
4.16	3.01	20.4	4.90
5.20	3.01	25.2	4.85

Solvent : 50% HOAc-50% H₂O (v/v) Temp. : 40° C

[HClO₄] : 0.1 M $k' = k_0/[\text{ketone}]$

(k_0 is the rate coefficient for the zero order disappearance of CBT)

Table 2. Effect of hydrogen ion concentration

[H ⁺] M	10 ⁷ k ₀ mol l ⁻¹ s ⁻¹		10 ⁶ k ₁ ' s ⁻¹	
	HClO ₄ *	H ₂ SO ₄ **	HClO ₄ *	H ₂ SO ₄ **
(a) Acetone				
0.05	2.74	3.67	5.48	7.33
0.10	5.56	7.29	5.56	7.29
0.15	8.04	10.8	5.36	7.20
0.20	10.55	14.5	5.28	7.25
0.24	12.5	...	5.20	...
* [CBT] : 2.37 × 10 ⁻³ M [A] : 2.57 × 10 ⁻² M				
** [CBT] : 3.22 × 10 ⁻³ M [A] : 3.34 × 10 ⁻² M				
(b) Acetophenone				
0.05	1.35	1.56	2.70	3.12
0.10	2.64	3.09	2.64	3.09
0.20	4.77	6.03	2.40	3.02
0.30	...	9.33	...	3.11
0.40	10.4	...	2.51	...
* [CBT] : 2.93 × 10 ⁻³ M [B] : 3.03 × 10 ⁻² M				
** [CBT] : 3.22 × 10 ⁻³ M [B] : 3.22 × 10 ⁻² M				
(c) Cyclopentanone :				
0.10	16.6	...	16.4	...
0.15	24.0	...	16.0	...
0.20	34.4	...	17.2	...
* [CBT] : 3.04 × 10 ⁻³ M [C] : 3.47 × 10 ⁻² M				

Solvent : 50% HOAc-50% H₂O (v/v) Temp. : 40° C
k₁' = k₀/[acid]

Table 3. Catalysis by acids on acetone system.

[H ⁺] M	Time in min for 50% reaction		
	HClO ₄	H ₂ SO ₄	HCl
0.05	65	70	34
0.10	35	40	19

Solvent : 50% HOAc-50% H₂O (v/v) Temp. : 40° C
[CBT] : 3.12 × 10⁻³ M [acetone] : 3.28 × 10⁻² M

However, all other conditions remaining the same, for a given concentration hydrochloric acid accelerates the reaction more than sulphuric or perchloric acids (table 3). This is traceable to a cumulative catalysis by H^+ and Cl^- . Such accelerations by HCl have been reported in the chlorination of phenols (Balasubramanian and Thiagarajan 1975) and oxidation of secondary alcohols by chloramine-T (Natarajan and Thiagarajan 1975) and N-chlorosuccinimide (Srinivasan and Venkatasubramanian 1973).

4.2 Effect of added salts

The addition of a neutral salt such as sodiumperchlorate does not produce any appreciable change in rate. But the addition of sodium chloride in presence of a mineral acid, not only enhances the rate but brings about a change in the rate picture itself. This is discussed in a later section. However, the effect of initially added chloride, in the absence of any mineral acids is not as much as it is in the presence of acid (tables 4 and 11). For example at $[NaCl] = 0.053 M$,

Table 4. Effect of added sodium chloride in the absence of mineral acid.

$[NaCl] 10^2 M$	$10^5 k_1 s^{-1}$
Nil	very slow
2.2	7.83
5.3	12.2
8.8	16.8
5.3	75.3*

* in presence of 0.1 M $HClO_4$ Temp.: 40° C
 Solvent: 50% HOAc-50% H_2O (v/v) [Acetone]: $3.28 \times 10^{-2} M$
 [CBT]: $3.26 \times 10^{-3} M$

k_1 is the rate constant for the first order loss of CBT in presence of initially added Cl^- .

Table 5. Kinetic isotope effect.

[substrate] $10^2 M$	$10^8 k_0$ mol $l^{-1} s^{-1}$	$10^6 k'_1$ s^{-1}	$k'_{1(H)}/k'_{1(D)}$
Acetone			
2.55	50.7	19.9	6.6
3.18	63.4	19.9	
Acetone- d_6			
2.56	7.48	2.90	3
3.19	9.58	2.97	

Solvent: 50% HOAc-50% H_2O (v/v) Temp.: 40° C
 [$HClO_4$]: 0.1 M [CBT]: $3.19 \times 10^{-3} M$
 $k'_1 = k_0/(\text{ketone})$

the rate constants for the first order loss of CBT in the absence and in the presence of perchloric acid are $1.22 \times 10^{-4} \text{ s}^{-1}$ and $7.53 \times 10^{-4} \text{ s}^{-1}$ respectively.

4.3 Kinetic isotopic effect

The chlorination of acetone- d_6 by CBT is a smooth reaction. The order with respect to the substrate was obtained by varying its initial concentration, as also by a plot of $\log k_0$ vs $\log [\text{substrate}]$, whose slope is unity. The chlorination of acetone- d_6 proceeds about 6.6 times slower than that of acetone itself (table 5) such a reasonable value (Reitz and Kopp 1939) for the primary kinetic isotope effect is indicative of a rate-determining enolisation step (Reitz 1937).

Table 6. Effect of solvent composition on rate.

HOAc-H ₂ O % (v/v)	$10^7 k_0 \text{ mol l}^{-1} \text{ s}^{-1}$		
	(a)	(b)	(c)
40-60	6.74	2.22	5.90
50-50	7.00	2.48	6.71
60-40	10.4	2.97	7.43
70-30	13.7	3.74	...
80-20	...	5.15	...

[HClO₄]: 0.1 M [CBT]: 3.17×10^{-3} M Temp.: 40° C
 (a) [acetone]: 3.27×10^{-2} M (b) [Acetophenone]: 3.20×10^{-2} M
 (c) [Isobutylmethylketone]: 3.31×10^{-2} M

Table 7. Effect of Structural variations.

Substrate	$10^5 k'_1 \text{ s}^{-1}$
Acetone	1.99
Acetone- d_6	0.30
Ethylmethylketone	2.54
Isobutylmethyl ketone	2.03
3,3, dimethyl but-2-one	1.14
Acetophenone	0.76
Propiophenone	0.33
Cyclopentanone	4.73
Cyclohexanone	12.9
Cycloheptanone	2.51
Cyclooctanone	21.1

Solvent: 50% HOAc-50% H₂O (v/v) Temp.: 40° C
 [HClO₄]: 0.1 M [CBT]: 3.20×10^{-3} M
 [Substrate]: 3.20×10^{-2} M $k'_1 = k_0/[\text{ketone}]$

4.4 Effect of solvent composition on rate

The rate of chlorination of ketones is dependent on the composition of the solvent medium used. Thus, in aqueous acidic media, increasing volume percentages of acetic acid increases the rate (table 6).

4.5 Effect of variations in the structure of the substrate

A wide range of variation in the substrate moiety has been employed to investigate the importance of structural effects in these reactions. A representative selection of aliphatic, aralkyl and alicyclic ketones has been used and the rate data presented (table 7). The results of the acetophenone-CBT reaction have been cast into a Hammett plot of $\log k_1'$ vs σ and the reaction constant ρ at 40° C is found to be -0.57 (table 8).

4.6 Effect of added benzotriazole

In the halogenation of phenols, anilides and toluenes by CBT (Srinivasan 1977), benzotriazole (BTH) which is one of the products of the reaction, when initially added produced a marked rate retardation accompanied by a change in the rate picture itself. Similar effects have also been reported in the oxidation of benzylalcohols by CBT (Rangadurai 1978). In the present investigation, however, initial addition of BTH produced only a small retardation and this is not attended by any change in the order on [CBT] or [Ketone]. Also, initial addition of BTH, brings about only a small retardation in rate even when the reaction is carried out in presence of chloride ions (table 9).

4.7 Activation parameters

The kinetics have been investigated in the temperature range 30° to 50° C. The rate constants and the activation parameters (as evaluated from plots of $\log k_1'$ vs T^{-1}) are presented in table 10. The isokinetic relationship has been tested for in the light of Exner's statistical treatment (Exner 1964, 1970). A plot of $\log k_{45^\circ}$ vs $\log k_{30^\circ}$ is linear indicating the operation of this relationship. The value of the isokinetic temperature calculated from the slope of the line is 64.6° K. The linear relationship (Bowden *et al* 1964) in the Exner plot is suggestive of a unified mechanism for all the compounds. Since the isokinetic temperature is well below the reaction temperature, the application of Hammett's equation is justified and with increase in temperature, the reaction constant may be expected to increase. Indeed such an increase is observed for the chlorination of acetophenones ($\rho = -0.53, -0.57$ and -0.63 at 30°, 40° and 50° C respectively). A plot of ΔH^\ddagger vs ΔS^\ddagger is also linear giving a value of 285° K for the isokinetic temperature, which is near the experimental temperature and this could arise out of an error slope. It may be pointed out that this value is markedly different from the one obtained by Exner's method. This only emphasises the caution that must be exercised in making such plots between two mutually dependent quantities (Exner 1973) (*viz* ΔH^\ddagger and ΔS^\ddagger).

Table 8. Evaluation of the reaction constants for substituted Acetophenones.

x-	σ	$10^8 k_1' s^{-1}$
H	O	7.60
<i>p</i> -NO ₂	+0.78	3.28
<i>m</i> -NO ₂	+0.71	2.70
<i>p</i> -CH ₃	-0.17	10.8
<i>p</i> -Cl	+0.23	6.35
<i>m</i> -Cl	+0.37	4.38
<i>p</i> -COCH ₃	+0.50	5.06

Solvent : 50% HOAc-50% H₂O (v/v) Temp. : 40° C
 [HClO₄] : 0.1 M [x-C₆H₄-COCH₃] : 3.26 × 10⁻² M [CBT] : 3.17 × 10⁻³ M
 σ values are taken from J Hine, *Physical organic chemistry*, McGraw-Hill Book Co.,
 New York, 1962, p. 87
 Correlation coefficient : 0.975 ; $\rho = -0.57$ $k_1' = k_0/[\text{ketone}]$

Table 9. Effect of added Benzotriazole.

BTH) 10 ³ M	10 ⁷ K ₀ mol l ⁻¹ s ⁻¹		
	*Acetone	**Ethylmethyl ketone	***Acetophenone
(a) Nil	7.00	8.23	2.48
1.82	...	6.83	2.34
2.97	5.92
3.63	...	6.56	2.34
4.95	5.75
5.45	...	6.61	2.36
6.93	5.70
7.26	...	6.60	...
(b) Nil	7.53†
3.60	7.02†
6.00	6.84†
8.40	6.52†

†10⁴ k₁s⁻¹ in presence of initially added chloride [Cl⁻] : 0.053 M
 Solvent : 50% HOAc-50% H₂O (v/v) Temp. : 40° C [HClO₄] : 0.1 M
 [CBT] : 3.15 × 10⁻³ M [*Acetone] : 3.29 × 10⁻² M
 ** [Ethylmethylketone] : 3.25 × 10⁻³ M ; *** [Acetophenone] : 3.23 × 10⁻² M
 (a) in the absence of Cl⁻ ; (b) in presence of Cl⁻

Table 10. First order rate constants and activation parameters for the Chlorination of ketones by CBr in 50% HOAc-50% H₂O (v/v).

Substrate	$10^6 k_1 \text{ s}^{-1}$								(i)	(ii)	(iii)	(iv)
	30°C	35°C	40°C	45°C	50°C	(i)	(ii)	(iii)				
Acetone	9.79	17.1	19.9	41.0	61.1	17.8	17.2	-25.2	25.1			
Acetone- <i>d</i> ₆	0.94	11.70	3.01	5.58	...	22.5	21.8	-14.2	26.3			
Ethylmethyl ketone	6.89	12.2	25.4	46.0	...	24.3	23.7	-3.97	24.9			
Isobutyl methyl ketone	4.80	8.19	20.3	38.1	...	26.5	25.9	+2.66	25.1			
3,3-dimethyl but-2-one	3.87	6.70	11.4	20.0	...	20.8	20.2	-16.7	25.4			
Acetophenone	2.63	4.42	7.60	13.2	21.4	21.1	20.5	-16.2	25.5			
<i>p</i> -chloroacetophenone	2.40	4.00	6.37	10.2	...	18.4	17.8	-25.6	25.8			
<i>m</i> -chloroacetophenone	1.56	2.68	4.45	7.76	...	19.7	16.1	-13.8	23.4			
<i>p</i> -Nitroacetophenone	1.14	...	3.30	5.62	9.35	21.1	20.4	-18.5	26.2			
<i>m</i> -Nitroacetophenone	1.02	2.71	4.68	7.82	...	21.4	20.8	-17.8	26.3			
<i>p</i> -Methyl acetophenone	3.42	5.97	10.9	19.5	...	21.6	21.0	-14.8	25.5			
<i>p</i> -Acetylacetophenone	3.63	6.20	10.3	17.0	...	19.6	19.0	-20.9	25.5			
Propiophenone	1.49	...	3.34	4.63	7.14	15.4	14.8	-36.6	26.2			
Cyclopentanone	13.7	23.0	47.3	81.6	...	26.1	25.5	+2.91	24.6			
Cyclohexanone	48.8	82.3	129	207	...	18.3	17.7	-19.9	23.9			
Cycloheptanone	18.93	15.5	25.7	43.8	...	20.3	19.6	-17.0	24.9			
Cyclooctanone	77.2	120	212	334	...	19.0	18.4	-16.8	23.6			

(i) E_{a} (kcal mol⁻¹) (ii) ΔH^\ddagger (kcal mol⁻¹) (iii) ΔS^\ddagger (kcal deg⁻¹ mol⁻¹) (iv) ΔG^\ddagger (kcal mol⁻¹)

Table 11. Effect of added sodium chloride.

[Substrate] 10^2 M	[NaCl] 10^2 M	$10^4 k_1 s^{-1}$
(a) Acetone :		
3.25	10.9	9.21
3.25	8.70	8.13
3.25	5.30	7.53
2.68	5.30	66.65
4.02	5.30	8.61
4.69	5.30	9.08
(b) Acetone- d_6 :		
3.19	5.30	4.00
3.83	5.30	4.21
4.47	5.30	4.56
(c) Ethylmethyl ketone :		
3.25	10.9	10.7
3.25	8.70	9.81
3.25	5.30	9.17
3.25	2.20	6.11
2.60	5.30	7.90
3.91	5.30	9.45
(d) Acetophenone :		
3.20	8.00	7.07
3.20	5.30	5.99
3.20	2.00	4.03
2.52	5.30	5.13
4.40	5.30	6.74

Solvent : 50% HOAc-50% H₂O (v/v); [HClO₄] : 0.1 M Temp. : 40° C

[C_{BT}] : 3.32×10^{-3} M

k_1 is the first order rate constant for the disappearance of C_{BT}.

4.8 Effect of added chloride on rate in mineral acid medium

Initially added chloride, apart from enhancing the rate, changes the rate law itself. In the presence of chloride the order with respect to [C_{BT}] changes to unity (it is zero in the absence of chloride) and that with respect to [ketone] becomes fractional (0.6 for acetone). The dependence on the concentration of chloride itself is fractional (0.3) (table 11). The order on acetone and chloride were obtained respectively from plots of $\log k_1$ vs \log [acetone] and $\log k_1$ vs \log [Cl⁻], where k_1 stands for the rate constant for the first order loss of C_{BT} in the presence of added chloride.

4.9 Effect of added sodiumacetate on rate

While the reaction is extremely sluggish in the absence of acetate, its addition in the concentration range 0.02M-1.0M has a pronounced accelerating effect. It is interesting to note that the reaction in presence of added acetate, is still first

Table 12. Effect of added Sodium acetate.

[Substrate] 10 ² M	[NaOAc] 10 ² M	10 ³ k ₀ mol l ⁻¹ s ⁻¹
(a) Acetone :		
3·20	Nil	6·30
3·20	80·0	29·2
3·20	40·0	19·8
3·20	20·0	14·2
3·20	2·54	9·8
3·99	2·54	11·9
4·99	2·54	14·7
(b) Acetophenone :		
3·15	Nil	3·98
3·15	2·55	5·47
3·15	7·65	6·55
3·15	5·10	7·88
3·78	5·10	7·89
4·40	5·10	9·31
2·52	5·10	5·32

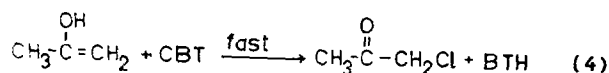
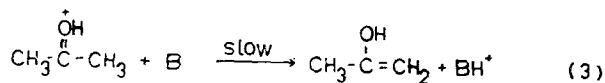
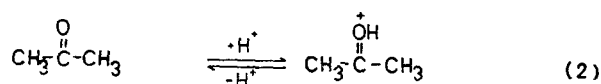
Solvent : 50% HOAc-50% H₂O (v/v) ; Temp. : 40° C [CBT] : 3·20 × 10⁻³ M

order with respect to ketone and zero order with respect to CBT. There is, however, a fractional order dependence (0·30-0·50) on [acetate], for the halogenation of acetone and acetophenone (table 12). The order on [acetate] has been obtained from a plot of log *k*₀ vs log [acetate].

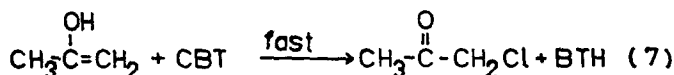
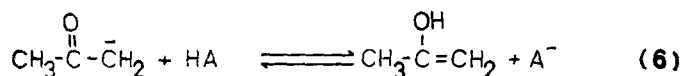
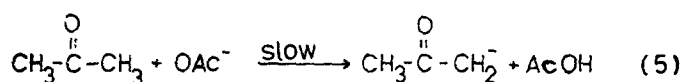
4.10 Mechanism of halogenation in the absence of chloride

4.10a: The halogenation of ketones by molecular halogen is usually catalysed both by acids and bases. However, the reaction between ketones and CBT could not be studied under alkaline conditions due to solubility limitations. The rate law under acidic conditions is given by equation (1). The zero order on the halogenating agent is in conformity with the usual kinetic picture namely a slow rate-determining formation of the enol followed by a fast attack of the halogenating species. This rate of attack is faster than the rate at which the enol reverts to the ketone. The catalysis by acids is ascribed to the preequilibrium "Proton transfer" shown in scheme I. The enhanced rate encountered in the case of HCl could be attributed to a cumulative and concurrent catalysis by both H⁺ and Cl⁻ (However, the addition of Cl⁻ alters the kinetic picture).

That the enolisation of the ketone is rate-determining in these reactions is corroborated by the fact that there is a primary kinetic isotope effect of magnitude 6·6 (for acetone and acetone-d₆). Similar effects have been reported (Balasubramanian and Thiagarajan 1976) in the chlorination of ketones with other N-halocompounds.

SCHEME I

(B = Base ; CBT = 1-chlorobenzotriazole ; BTH = Benzotriazole)

SCHEME II

HA = Acid

The enolisation of ketones has been shown to be a general acid-base catalysed reaction (Bell 1973). In acetic acid-acetate buffer systems, the catalysis by both acetate and acetic acid have to be taken into account. The generalised rate expression of the form

$$\text{rate} = \{k_{\text{H}_2\text{O}} [\text{H}_2\text{O}] + k_{\text{H}^+} (\text{H}^+) + k_{\text{OH}^-} [\text{OH}^-] + k_{\text{HOAc}} [\text{HOAc}] + k_{\text{OAc}^-} [\text{OAc}^-]\} [\text{Ketone}] \quad (8)$$

has been reported (Dawson and Spirey 1930 ; Bell and Jones 1953) for such a situation.

Assuming a general acid-base catalysed enolisation for the chlorination of ketones by CBT, by the proper choice concentrations of catalysing species and by a regression analysis of the rate data using a micro 2200 Hindustan Computer, the catalytic coefficients have been calculated. The following approximations have been made in these calculations. (i) the catalysis due to water and hydroxide

ion are negligible and remain constant throughout and (ii) from the pH value of the buffered solutions, the $[\text{OAc}^-]$ may be calculated using the K_a value for HOAc to be valid in such high concentrations of acetic acid.

k_{H^+} was first evaluated using rate constants at high $[\text{H}^+]$ where it may be assumed that catalysis by H^+ would be the predominant one. Employing these k_{H^+} values and the rates in buffered HOAc– H_2O media, k_{OAc^-} was evaluated. Utilising the value of k_{H^+} and k_{OAc^-} and the rate data for the variation of HOAc in the solvent media k_{HOAc} was evaluated. This procedure was repeated several times from k_{H^+} onwards, by correcting for the catalysis of OAc^- and HOAc in acid media, until two successive determinations gave reproducible values. Thus,

$$\text{rate} = \{k' [\text{C}] + 4.48 \times 10^{-6} [\text{H}^+] + 1.68 \times 10^{-7} [\text{OAc}^-] + 9.09 \times 10^{-9} [\text{HOAc}]\} [\text{Ketone}] \quad (9)$$

where $k' [\text{C}]$ represents the total contribution of OH^- and solvent water. It may be noticed that the values of the calculated catalytic coefficients are comparable to those obtained by earlier workers (Bell and Jones 1953). The rate law reported by Bell and Jones is

$$\text{rate} = \{8.33 \times 10^{-13} [\text{H}_2\text{O}] + 2.68 \times 10^{-6} [\text{H}^+] + 2.5 \times 10^{-2} [\text{OH}^-] + 8.33 \times 10^{-8} [\text{HOAc}] + 2.50 \times 10^{-7} [\text{OAc}^-]\} [\text{Ketone}] \quad (10)$$

The high value for the catalytic coefficient of H^+ point to the fact that at high acidities the second term in equation (9) is dominant, accounting for the observed first order dependence on $[\text{H}^+]$. Any increase in $[\text{OAc}^-]$ is accompanied by a gradual and corresponding decrease in $[\text{H}^+]$. The fractional order obtained on $[\text{OAc}^-]$ may be due to the combination of the two effects *viz* an enhanced catalysis by OAc^- and an opposing reduction in the catalysis by H^+ by concentration effects.

The chlorinating species reacting with the enolic form of the ketone could be either CBT itself or species derived from it like CBT H^+ , Cl^+ , HOCl , H_2OCl^+ and ClOAc . However, in view of the independence of rate on the initial concentration of CBT these species become kinetically indistinguishable.

4.10b. *Structural effect*: As the rate is dependent only on the rate of enolisation under these conditions, any change in rate could be attributed only to the ease or otherwise of enolisation. For example, in the case of alicyclic ketones, it is noticed (table 7) that those with odd number of carbon atoms get chlorinated slower than those with even number. It has been reported that alicyclic ketones with even number of carbon atoms have a greater enolic content than their adjacent analogues with odd number of carbon atoms (Gero 1961 ; Alinger *et al* 1967) though reports contrary to this have also been made indicating that the enol of cyclohexanone, for example is less stable than that of cyclopentanone (Bell and Smith 1966 ; Hine 1975).

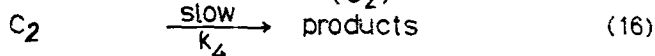
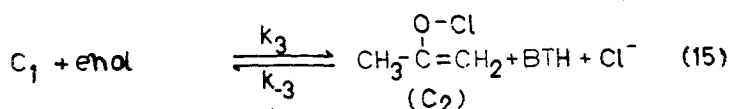
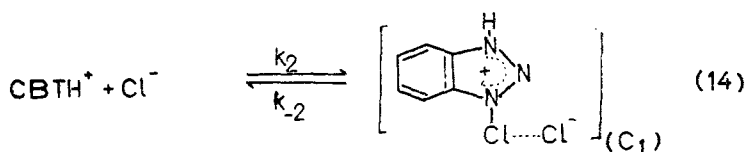
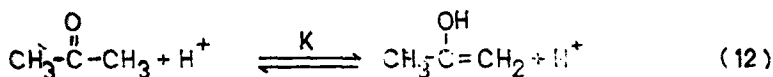
The Hammett ρ value of -0.57 obtained for the acetophenone series indicates only a small structural influence on rate. A negative ρ value is associated with the development of a positively charged carbon centre at the site of the reaction

in the transition state. However, since the present reaction involves a protonation followed by a deprotonation, the ρ value results only from the over all contribution by the substituents to these opposing processes. A value of $\rho = -0.6$ has been reported for the bromination of substituted benzyl phenyl ketones.

4.10c. *Mechanism of halogenation in the presence of chloride ions* : It is significant to point out that the rate law, in the presence of chloride ions, is

$$-\frac{d[\text{CBT}]}{dt} = k' [\text{CBT}] [\text{H}^+] [\text{acetone}]^{0.6} [\text{Cl}^-]^{0.2} \quad (11)$$

This might mean that CBT and Cl^- interact to produce a steady and small concentration of another halogenating species (C_1), which then interacts with the substrate in its enolic form to give the products *via* a complex (C_2) *viz* the enol hypochlorite (scheme 3) (For acetone- d_6 under these conditions the kinetic picture is retained except for a lowered order dependence on the substrate).



SCHEME III

(Note : The k_2 in equation 14 is different from the one given in equation 1)

From scheme 3,

$$\text{Rate} = k_4 [\text{C}_2] \quad (17)$$

applying steady state approximation to (C_1) and (C_2)

$$[\text{C}_1] = \frac{k_2 [\text{CBTH}^+] [\text{Cl}^-]}{\{k_{-2} + k_3 [\text{enol}]\}} + \frac{k_{-3} [\text{C}_2] [\text{BTH}] [\text{Cl}^-]}{\{k_{-2} + k_3 [\text{enol}]\}} \quad (18)$$

$$[C_2] = \frac{k_2 k_3 [\text{enol}] [\text{CBTH}^+] [\text{Cl}^-]}{\{k_4 + k_{-3} [\text{BTH}] [\text{Cl}^-]\} \{k_{-2} + k_3 [\text{enol}]\} - \{k_3 [\text{enol}] \times k_{-3} [\text{BTH}] [\text{Cl}^-]\}} \quad (19)$$

$$\text{Rate} = \frac{k_2 k_3 k_4 [\text{enol}] [\text{CBTH}^+] [\text{Cl}^-]}{k_{-2} k_4 + k_3 k_4 [\text{enol}] + k_{-2} k_{-3} [\text{BTH}] [\text{Cl}^-]} \quad (20)$$

This equation predicts fractional order dependences for rate on both [ketone] and [Cl⁻] and a first order dependence on [CBT], all of which have been realised [rate law as per equation (11)]. There is a definite but small retardation with added benzotriazole (table 9, b) which is also in consonance with equation (20).

Further as per (20), the reciprocal of rate should be linearly related to (i) the reciprocal of [enol] when [CBT], (H⁺), (Cl⁻) and (BTH) are not varied and (ii) the reciprocal of [Cl⁻] when [CBT], [H⁺], [enol] and [BTH] are not varied. This has been tested out by plotting 1/k₁ vs 1/[enol] (c.c. = 0.999) as also 1/k₁ vs 1/Cl⁻ (c.c. = 0.999); both are linear with clear Y-intercepts which also indicates "Complex formation" (the chlorination of acetone-d₆ by CBT in the presence of chloride is also first order in CBT but exhibits a fractional order dependence (0.3) on [acetone-d₆]. Similar results have been obtained (Balasubramanian 1976) in the chlorination of acetone-d₆ by chloramine-T. A plot of 1/k₁ vs 1/[acetone-d₆] also yields a straight line with a clear Y-intercept (c.c. = 0.976). The k₁ involved in the above plots is the rate constant for the first order disappearance of CBT.

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