Indian Journal of Chemistry
Vol. 28A, April 1989, pp. 288-291

Kinetics & Mechanism of Acid Bromate Oxidation of Aliphatic, Aralkyl & Alicyclic Ketones

N KRISHNA MURTHY†, CH SANJEEVA REDDY & E V SUNDARAM*
Department of Chemistry, Kakatiya University, Warangal 506 009
Received 9 *February* 1988; *revised* 25 *May* 1988; *accepted* 13 *June* 1988

Oxidation of a few typical aliphatic, aralkyl and alicyclic ketones with acid bromate has been investigated. The reaction is first order in both [bromate] and [ketone]. The rate increases with increase in [acid] of the medium. Ionic strength effect is marginal but, the oxidation rates are susceptible to change in dielectric constant of the medium. The mechanism proposed involves the attack of acid bromate on the enol-form of the ketone in the rate-determining, formation of an intermediate followed by a fast decomposition to products. The order of reactivities is: (i) ethyl methyl ketone > *n*-propyl methyl ketone > dimethyl ketone for simple aliphatic ketones; (ii) acetophenone > propiophenone > butyrophenone for aralkyl ketones; and (iii) cyclooctanone > cyclohexanone > cycloheptanone for alicyclic ketones. Thermodynamic parameters have been evaluated and discussed.

Oxidation of aliphatic and aralkyl ketones in acidic and alkaline media has been extensively studied using both one and two-electron oxidants[1-8]. Since the keto-form of a ketone is always in equilibrium with the corresponding enol-form, and depending upon the oxidant it can attack either the keto[1-3] or the enol-form[4-8]. A variety of oxidation products have also been reported in the oxidation of aliphatic and aralkyl ketones by a variety of oxidants[4,6,8-10]. Similar studies using acid bromate as an oxidant are lacking, hence the title investigation.

Materials and Methods

All the chemicals used were of either LR or AR (BDH/E Merck/Fluka) grade and were further purified by either distillation or recrystallization. Purified acetic acids (AR, BDH) was used. Titrimetric procedure was followed to determine the rate constants which are reproducible within ±3%. Liberation of Br_2 (from an auto-catalytic reaction) was suppressed employing mercury(II) acetate.

Results and Discussion

Under the psuedo-first order conditions, $[Br(V)]_o << [substrate]_o$, the plot of $\log[Br(V)]_t$ against time was linear upto three-half lives, indicating the order in (Br(V)] to be unity. But, the pseudo-first order rate constants (k') decreased with increase in $[bromate]_o$. A similar observation was also recorded in the acid bromate oxidation of pinacol[11], olefinic acids[12] and *tert*-alcohols[13]. The decrease in rate was explained by assuming the bromate dimer which was inactive towards reduction. At low [acid], k' remained practically constant but, at higher [acid] the k' value decreased with increase in [oxidant]. The magnitude of decrease in k' was expected to be more at higher [acid]. Hence, in the present study rate parameters were studied at one particular [bromate].

An increase in [substrate] increased the reaction rate (Table 1). The plots of log k_{obs} versus log[substrate] were linear with unit slopes indicating first order dependence in [substrate]. Further, the values of k_2 ($=k_{obs}/[sub]$) were almost identical confirming first order dependence in [ketone]. the reaction rates were facilitated by an increase in $[H_2SO_4]$. The plots of log k' versus 1/D were linear with positive slopes. From the slopes of linear plots of log k_2 versus 1/T, the Arrhenius activation parameters were computed and are recorded in Table 2. The reaction system did not induce polymerisation of added acrylonitrile thus ruling out the involvement of free radicals. Carboxylic acids were the final products of oxidation and were identified by usual tests.

Mechanism and rate law

The experimental observations suggest the rate law (1)

$$-d[Br(V)]/dt = k_2[ketone][Br(V)].h_o \quad \ldots(1)$$

It is well established that halogenation of ketones proceeds via rate-controlling enolisation process. The fact that the oxidation rate of ketone with bromate is slower than that of halogenation and

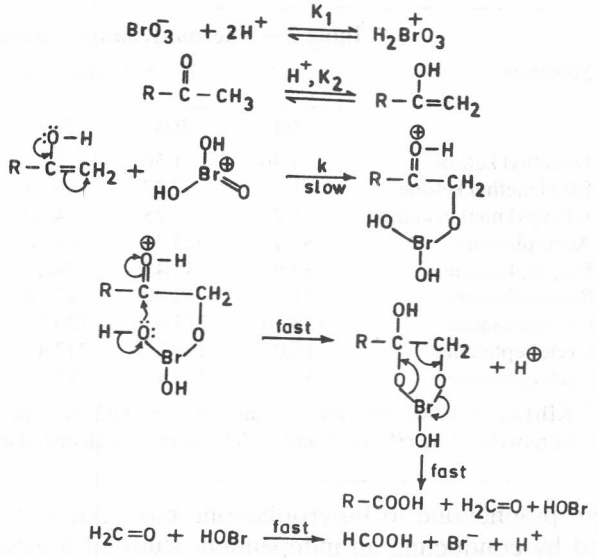
†CKM Arts & Science College, Warangal

Table 1—Dependence of Rate on [Ketone] in Acid Bromate-Ketone System*

Substrate	[Substrate] (mol dm^{-3})	$10^4 \times k_{obs}$ (s^{-1})	$10^4 \times k_2 \{= k_{obs}/[S]\}$ ($dm^3\ mol^{-1}\ s^{-1}$)
Dimethyl ketone	0.01	0.026	2.60
	0.02	0.051	2.55
	0.03	0.078	2.60
	0.04	0.105	2.62
	0.05	0.131	2.62
	0.10	0.261	2.61
Ethyl methyl ketone	0.01	0.16	16.00
	0.02	0.33	16.50
	0.03	0.49	16.33
	0.04	0.65	16.25
	0.05	0.82	16.40
	0.10	1.62	16.20
n-Prophy methyl ketone	0.01	0.15	11.50
	0.02	0.23	11.50
	0.03	0.35	11.67
	0.04	0.46	11.50
	0.05	0.56	11.20
	0.10	1.15	11.50
Acetophenone[a]	0.01	1.12	112.00
	0.02	2.27	113.50
	0.03	3.34	111.33
	0.04	4.44	111.00
	0.05	6.64	110.67
	0.10	11.23	112.30
Propiophenone	0.01	0.98	98.00
	0.02	1.98	99.00
	0.03	2.96	98.67
	0.04	3.92	98.00
	0.05	4.84	96.80
	0.10	9.89	98.90
Butyrophenone	0.01	0.51	51.00
	0.02	1.03	51.50
	0.03	1.54	51.33
	0.04	2.06	51.50
	0.05	2.58	51.60
	0.10	5.18	51.80
Cyclohexanone	0.01	5.61	561.0
	0.02	11.14	557.0
	0.03	17.60	586.6
	0.04	22.17	554.3
	0.05	27.52	550.4
	0.10	55.86	558.6
Cycloheptanone	0.01	2.90	290.0
	0.02	5.76	288.0
	0.03	8.75	291.0
	0.04	11.51	287.8
	0.05	11.41	288.4
	0.10	28.96	289.6
Cyclooctanone	0.01	7.92	792.0
	0.02	16.12	806.0
	0.03	23.89	789.7
	0.04	31.99	799.7
	0.05	39.90	799.6
	0.10	79.64	796.4

(*)$[KBrO_3]$ = 2.0 × 10^{-3} mol dm^{-3}; $[H_2SO_4]$ = 2.0 mol dm^{-3}; HOAc-H_2O = 1:1 (v/v); $[Hg(OAc)_2]$ = 0.01 mol dm^{-3}; temp = 40°C

[a]at 30°C



Scheme 1

that the reaction exhibits first order dependence in [oxidant] rule out the enolisation step being the rate-determining step. Bromate, being a two-electron oxidant, attacks the enol form of the ketone[1]. With these facts a possible mechanism, showing the attack of the oxidant on the enol form, may be given as in Scheme 1. In this mechanism, the active species of the oxidant is $H_2^+BrO_3$, in confirmity with the literature evidence[11–15].

The order of reactivities for aralkyl ketones is found to be acetophenone > propiophenone > butyrophenone. This sequence can be explained as follows: In accordance with Scheme 1 enolisation step involves equilibrium protonation followed by deprotonation from the α-carbon atom. These two steps affect the enolisation process depending on the structural factors. In propiophenone the methyl group enhances the electron-density at the carbon atom adjacent to the carbonyl group due to inductive effect. Therefore, the ease of deprotonation from that carbon atom in proprophenone decreases as compared to that in acetophenone. This should result in the decrease in the enolic content of propiophenone and subsequently to a decrease in the rate, as is actually observed. And also the +I effect of the methyl group in propiophenone opposes the π-electrons of C=C polarisation compared to that in acetophenone. Therefore the attack of electrophile is less facile and hence the observed decrease in the rate. In the case of butyrophenone due to the presence of C_2H_5 the +I effect becomes more pronounced, resulting in a further decrease in the oxidation rate. This decreased trend in the case of enolisaltion on passing from acetophenone to

Table 2—Thermodynamic Parameters for Acid Bromate-Ketone Systems*

Substrate	$10^4 \times k_2$ (dm^3 mol^{-1} s^{-1}) at K					$\Delta H^{\neq}$ (kJ mol^{-1})	$-\Delta S^{\neq}$ (Jk^{-1} mol^{-2})	$\Delta G^{\neq}$ (kJ mol^{-1})
	298	303	308	313	318			
Dimethyl ketone	1.30	1.50	2.03	2.55	4.12	49.70	153.8	96.39
Ethyl methyl ketone	1.63	2.87	6.25	15.12	30.03	119.32	−80.9	94.76
n-Propyl methyl ketone	1.25	2.25	4.50	11.00	16.07	117.14	−71.8	95.41
Acetophenone	85.13	113.50	201.50	268.50	415.60	66.40	63.1	85.52
Propiophenone	33.92	45.45	74.11	99.07	167.10	64.49	77.2	87.87
Butyrophenone	31.54	38.02	47.53	51.54	67.09	36.16	163.9	85.83
Cyclohexanone	128.50	223.0	330.5	557.0	671.4	52.18	104.5	83.84
Cycloheptanone	115.0	147.2	217.4	288.0	398.2	54.92	98.9	84.90
Cyclooctanone	151.1	233.4	383.3	806.1	1274.5	88.43	−15.5	84.22

*[$KBrO_3$] = 0.002 mol dm^{-3}; [substrate] = 0.02 mol dm^{-3}; [H_2SO_4] = 2.0 mol dm^{-3}; HOAc-H_2O = 1:1 (v/v); [Hg(II)] = 0.01 mol dm^{-1}; $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ values are calculated at 303 K

propiophenone to butyrophenone has been verified by conducting an independent study of iodination of these ketones. The observed rate constants are 4.53×10^{-2}, 1.0×10^{-2} and 0.88×10^{-2} dm^3 mol^{-1} s^{-1} respectively[16]. These values indicate that the rate of enolisation decreases with increase in the carbon chain length adjacent to carbonyl group.

Amongst the simple aliphatic ketones studied the order of reactivities is ethyl methyl ketone > *n*-propyl methyl ketone > dimethyl ketone, which is in consonance with the enolisation rates[17].

The order of reactivities among the alicyclic ketones studied is: cyclooctanone > cyclohexanone > cycloheptanone. It is generally presumed that the most favoured conformation of cycloheptanone[18] is the twist chair form, which is responsible for the lowest rate observed. The investigations of Allinger *et al.*[19] and Leonard *et al.*[20] show that the cyclooctanone exists in the crown form though the spectral data are consistent with the chair form (νC=O at 1710 cm^{-1}). The differences in the reactivity between cyclooctanone and cycloheptanone are due to the existence of former in the crown form and the latter in the chair form. The results are quite consistent with the studies on the determination of enol contents of the cyclic alkanones[21] where it has been observed that the enol content (8 > 7) alternates with ring size.

The enolisation rate constants are reported[17] to be 4.73×10^{-5}, 12.9×10^{-5}, 2.51×10^{-5} and 21.1×10^{-5} s^{-1} respectively for cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone, respectively. The higher enolisation constant of cyclohexanone is probably the most important factor contributing towards greater reactivity of this ketone compared to that of cycloheptanone. In step (iii) (Scheme 1) there is a change in the hybridization in the ketone from sp^2 to sp^3 at the site of attack. The conversion from sp^2 into sp^3 is most favoured when it is a six-membered ring and least favoured when it is seven-membered ring[22]. The higher reactivity of cyclooctanone over cyclohexanone is a consequence of higher enolic content[23]. This trend can be seen in the rate data reported in Table 2. A different order of rectivities, viz. cyclohexanone > cyclopentanone > cyclooctanone > cycloheptanone has been observed in the vanadium(V) oxidation[24] where it is suggested that the preferential mechanistic route is via their keto-forms involving single electron transfer in the rate-determining step.

The free energy of activation ($\Delta G^{\neq}$) is nearly the same (90 ± 6 kJ/mol) and the isokinetic and Exner's plots are linear with r = 0.998 and 0.996 respectively, supporting the operation of an identical mechanism for all the ketones studied. Therefore it can be concluded that the slow step involves attack of the oxidant on the corresponding enol form giving rise to an intermediate (see Scheme 1) and this intermediate decomposes to form the products.

References

1 Littler J S, *J chem Soc*, (1962) 827.
2 Patnayak L N, Rout M K & Behra G, *Indian J Chem*, **9** (1971) 432.
3 Kelkar M S, Shankar R & Bakore G V, *Indian J Chem*, **13** (1975) 1093.
4 Radhakrishna Murthy P S & Pati S N, *Indian J Chem*, **17A** (1979) 97.
5 Radhakrishna Murthy P S & Prasada Rao M D, *Indian J Chem*, **15A** (1977) 524.
6 Manikyamba P, Raghunath Rao P & Sundaram E V, *J Indian chem Soc*, **60** (1983) 652.
7 Prasada Rao M, Sethuram B & Navaneeth Rao T, *Indian J Chem*, **19A** (1980) 582.

8 Khandual N C, Satpathy K K & Nayak P L, *Indian J Chem*, **11** (1973) 770.
9 Nath P & Banerji K K, *Can J Chem*, **48** (1970) 2415.
10 Radhakrishna Murthy P S & Prasada Rao M D, *Indian J Chem*, **17A** (1979) 60.
11 Sanjeeva Reddy Ch & Sundaram E V, *Int J chem Kinet*, **15** (1983) 307.
12 Sanjeeva Reddy Ch & Sundaram E V, *Gazz Chem Ital*, **113** (1983) 1177.
13 Sanjeeva Reddy Ch & Sundaram E V, *Indian J Chem*, **26A** (1987) 118.
14 Guttmann S & Anbar M, *J Am chem Soc*, **83** (1961) 4741.
15 Barton A F & Wright C A, *J chem Soc(A)*, (1968) 1747.
16 Krishnamurthy N, Ph D Thesis, Kakatiya University, Warangal (1986).
17 Sabesan A & Venkatasubramanian, *Indian J Chem*, **9** (1971) 942.
18 Allinger N L, *J org Chem*, **10** (1954) 328; **21** (1956) 915; *J Am chem Soc*, **79** (1957) 3443; **80** (1958) 1953.
19 Alinger N L & Greenberg S, *J Am chem Soc*, **84** (1962) 2394.
20 Leonard N J, Milligan T W & Brown T L, *J Am chem Soc*, **82** (1960) 4075.
21 Hendrickson J R, *J Am chem Soc*, **83** (1961) 4537; **84** (1962) 3355; *Tetrahedron*, **19** (1963) 1387.
22 Eliel E L, *Stereochemistry of carbon compounds*, Tata-McGraw Hill, New Delhi), (1975) 266.
23 Alinger N L, Chow L W & Ford R A, *J org Chem*, **32** (1967) 1994.
24 Radhakrishna Murthy P S & Devi S, *Indian J Chem*, **14** (1976) 399.