Oxidation of Aliphatic Ketones, Substituted Acetophenones & Cyclic Ketones by Potassium Permanganate

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Kinetics of oxidation by potassium permanganate of series of aliphatic ketones in aqueous medium, and of substituted acetophenones and cyclic ketones in aqueous acetic acid at constant ionic strength are reported. The reactions are first order each in the substrate and the oxidant. Change in acetic acid content of the solvent does not affect the kinetic rate. The order of reactivity is benzoyl acetone > acetoacetic ester > diisopropyl ketone > isobutyl methyl ketone > ethyl methyl ketone > acetone in aliphatic system and p-nitro > m-nitro > p-bromo > p-chloro > acetophenone > p-methyl in the case of substituted acetophenones, and cyclohexanone > cyclooctanone > cyclopentanone > cycloheptanone in cyclic ketones. The higher reactivity of cyclohexanone has been attributed to the higher enol content. Taft's and Hammets' plots give ρ values +5·7 and +3·75 for aliphatic ketones and aryl aliphatic ketones respectively. Thermodynamic parameters have been evaluated. A mechanism consistent with the results obtained is proposed.

K INETICS of oxidation of aliphatic ketones, aryl aliphatic ketones and cyclic ketones by various oxidants in alkaline media have been extensively studied[1-10]. This communication deals with the oxidation of a number of aliphatic, aryl aliphatic and cyclic ketones by potassium permanganate in acidic medium.

Materials and Methods

All the substrates used were of BDH (AR) grade and were redistilled or recrystallized before use. Stock solution of potassium permanganate (M & B) was prepared in doubly distilled water. Oxidation of aliphatic ketones was studied in aqueous medium and that of aryl aliphatic and cyclic ketones in aq. acetic acid. The pH was adjusted by using a buffer consisting of Na_2HPO_4 ($0·025M$)+H_3PO_4 (10%, v/v). The temperature was controlled within $\pm 0·02°$. Sodium pyrophosphate (Riedel) was used to keep ionic strength constant as well as to scavenge the intermediate valence states of manganese. The kinetics of the reaction was followed by standard iodometric method. Due correction was made due to solvent oxidation which was always less than 6%. The iodometric method for the estimation of MnO_4^- in organic oxidations wherein intermediate valence states of Mn like Mn(VI), Mn(V), Mn(IV), Mn(III) were involved to a variable degree, yielded a gross estimate of the total oxidizing ability of the oxidant. Two of the reduction products of Mn(VII) are MnO_2 and Mn^{2+}. The nature of reduction of Mn(VII) seems to be dependent on the vigour of the reducing agent. Keeping this in view many corrections have been applied[11,12]. In view of the limitations of the corrections suggested the rate constants, reproducible within 3% have been computed by the usual tangential method from the gross concentration of the oxidant.

Product analysis — In the acetophenone series the products are mainly the corresponding benzoic

acids. In aliphatic series the main product in all the cases is acetic acid which corroborates with the earlier work of Wiberg[8] where the major product is also acetic acid in the case of acetone. In case of cyclopentanone and cyclohexanone the products are succinic acid and adipic acid respectively.

Results and Discussion

The kinetic data are presented in Tables 1-3. The reactions are first order each in the substrate and oxidant. The order of reactivity of various

TABLE 1 — PSEUDO FIRST ORDER RATE CONSTANTS FOR THE OXIDATION OF ACETONE AND ACETOPHENONE AT 45°

{(1) Oxidation of acetone in aq. medium: [acetone] = $3·499 \times 10^{-3}M$; [MnO_4^-] = $1·976 \times 10^{-4}M$; [pyrophosphate] = $0·01M$; [Na_2HPO_4] = $2·5 \times 10^{-2}M$; H_3PO_4 = 10% (v/v). (2) Oxidation of acetophenone in acetic acid: [acetophenone] = $2·062 \times 10^{-3}M$; [MnO_4^-] = $1·809 \times 10^{-4}M$; [pyrophosphate] = $0·01M$; [Na_2HPO_4] = $0·025M$; [H_3PO_4] = 10% (v/v)}

t_m	$(b-x) \times 10^5$	k_1 (min^{-1}) $\times 10^5$
	ACETONE	
82·5	18·772	62·52
165	17·784	63·93
252	16·796	64·62
350	15·808	63·89
465	14·820	61·84
540	13·832	66·06
	ACETOPHENONE	
36	17·185	143·3
75	16·281	140·3
117·5	15·376	138·6
162·5	14·472	137·6
210	13·567	137·0
255	12·663	139·9

TABLE 2 — EFFECT OF [SUBSTRATE] ON THE REACTION RATE

{Solvent: water; [pyrophosphate] = 0·01M; [Na_2HPO_4] = 0·025M; H_3PO_4 = 10% (v/v); temp. = 45°}

[Substrate] 10^4M	$k_1 \times 10^4$ min	k_2 litre mole^{-1} min^{-1}
ACETONE, [MnO_4] = 1·965 × 10^{-4}M		
34·99	6·378	0·1824
43·10	8·279	0·1921
65·34	11·650	0·1782
ETHYL METHYL KETONE, [MnO_4] = 1·965 × 10^{-4}M		
29·80	18·89	0·6339
47·71	28·72	0·6012
66·31	40·93	0·6172
ACETOPHENONE*, [MnO_4] = 1·809 × 10^{-4}M		
10·35	6·984	0·6748
20·62	13·94	0·6761
34·06	23·57	0·6920
p-Me-ACETOPHENOE*, [MnO_4] = 1·809 × 10^{-4}M		
19·30	8·125	0·4209
27·12	11·41	0·4207
38·63	16·39	0·4243
CYCLOHEXANONE*, [MnO_4] = 2·216 × 10^{-4}M		
12·49	55·81	4·469
26·02	128·3	4·941
57·14	241·0	4·218
CYCLOHEPTANONE*, [MnO_4] = 2·216 × 10^{-4}M		
16·07	8·354	0·5768
24·56	14·37	0·5855
41·53	22·06	0·5311

*Oxidations were carried out in 20% HOAc (v/v) at 45°C.

TABLE 3 — SECOND ORDER RATE CONSTANTS FOR THE OXIDATION OF VARIOUS KETONES

{[Na_2HPO_4] = 0·025M; [H_3PO_4] = 10% (v/v); [MnO^-_4] = 1·976 × 10^{-4}M; [pyrophosphate] = 0·01M}

Substrate	k_2, litre mole^{-1} min^{-1}		
	35°	40°	45°
SOLVENT: WATER			
Acetone	0·0704	0·1142	0·1824
Ethyl methyl ketone	0·2209	0·4427	0·6339
Acetoacetic ester	74·50	98·86	145·5
Diisopropyl ketone	0·3888	0·4546	1·15
Isobutyl methyl ketone	0·2292	0·3184	0·7399
Benzoylacetone	312·3	468·1	747·3
SOLVENT: AQ. HOAc (20%, v/v)			
Acetophenone	0·3686	0·5919	0·6761
p-Nitroacetophenone	0·8076	1·324	1·708
m-Nitroacetophenone	0·5985	0·7444	1·324
p-Chloroacetophenone	0·4571	0·6020	0·7916
p-Bromoacetophenone	0·5131	0·7228	0·9945
p-Methylacetophenone	0·2915	0·3636	0·4209
Cyclohexanone	4·941	6·685	9·158
Cyclopentanone	0·8063	0·9975	1·727
Cycloheptanone	0·5855	0·7909	1·217
Cyclooctanone	1·978	2·803	4·268

ketones with respect to acetone as the standard is: benzoylacetone > acetoacetic ester > diisopropyl ketone > isobutyl methyl ketone > ethyl methyl ketone > acetone. The higher reactivity of benzoylacetone over acetoacetic ester is mainly due to the conjugation effect and the benzoyl group increases the relative thermodynamic stability of the enol. The reactivity order diisopropyl ketone > isobutyl methyl ketone > ethyl methyl ketone > acetone indicates that increase in the number of alkyl groups increases the rate, as alkyl groups increase the equilibrium enol content. This has been invoked in our earlier work of oxidation of ketones by hexacyanoferrate (III)[1].

In the oxidation of substituted acetophenones the order of reactivity is p-nitro > m-nitro > p-bromo > p-chloro > acetophenone > p-methyl. This indicates that electron withdrawing groups in the benzene ring facilitate the oxidation and electron releasing groups retard the process. The electron withdrawing groups increase the relative stability of the enol and hence the higher reactivity.

ρσ Relation

Employing the Taft substituent constants an attempt is made to correlate the structure and reactivity for acetone, acetoacetic ester, benzoylacetone and a ρ value of +5·7 was obtained, with correlation coefficient of 0·98 and standard deviation of +0·02. The data for ethyl methyl ketone, isobutyl methyl ketone, diisopropyl ketone could not be considered as there is no Taft substituent constant which has taken into account the conjugative ability of the alkyl groups as observed in these reactions. In the case of substituted acetophenones a plot of log k_2 versus σ is linear with a ρ value +3·75, correlation coefficient of 0·95 and standard deviation of +0·05, indicating that electron withdrawing groups accelerate the process.

The observed reactivity order in case of cyclic ketones is cyclohexanone > cyclooctanone > cyclopentanone > cycloheptanone. The higher reactivity of cyclohexanone is probably due to the terminal hydrogen of the nearly strainless puckered residue $(CH_2)_4$ in cyclohexene fulfilling the stereochemical requirements for hyperconjugation with the cyclic C=C groups better than does the terminal hydrogen of the nearly flat residue $(CH_2)_3$ in cyclopentene. This also explains the higher enol content for the cyclohexanone as compared to other medium ring ketones. The most favoured conformation of cycloheptanone is the twist chair form. This is responsible for the lower rate observed in the oxidation process.

Solvent Effect

Change in percentage of acetic acid does not affect the kinetic rate. This is unexpected and no satisfactory explanation could be offered. Similar finding was observed by Banerji et al.[13] in the oxidation of benzyl alcohol by acid potassium permanganate.

Effect of added salts — An increase in [sodium pyrophosphate] does not affect the kinetic rate significantly. Also the addition of sodium fluoride does not alter the rate. However, addition of

TABLE 4 — EFFECT OF ADDED SALTS

{$[Na_2HPO_4] = 0.025M$; $[H_3PO_4] = 10\%$ (v/v); $[MnO_4^-]$ = $1.976 \times 10^{-4}M$; temp. 45°}

Added salt	[Salt] × 10⁴ (M)	k_2, litre mole⁻¹ min⁻¹
ETHYL METHYL KETONE		
Sodium pyrophosphate	0.000	0.6442
	1.905	0.5450
	9.750	0.5594
	49.760	0.6200
	100.000	0.6339
Sodium fluoride	120.000	0.6372
K₂SO₄	100.000	0.5875
MnSO₄	6.622	0.5675
p-NITROACETOPHENONE		
MnSO₄	7.945	1.407*
	16.260	1.392*
	34.160	1.202*
NaF	108.300	1.680*
CYCLOHEXANONE		
MnSO₄	19.87	2.345†

*k_2 with 20% (v/v) acetic acid.
†k_2 with 20% (v/v) acetic acid and at 35°C.

TABLE 5 — THERMODYNAMIC PARAMETERS

Substrate	$\Delta E\ddagger$ kcal mole⁻¹	$\Delta H\ddagger$ kcal mole⁻¹	$\log_{10}A$ kcal mole⁻¹	$\Delta S\ddagger$ e.u.
Acetone	17.8	17.1	9.69	−16.3
Ethyl methyl ketone	22.9	22.2	13.8	+2.3
Diisopropyl ketone	22.9	22.2	14.05	+2.7
Isobutyl methyl ketone	22.9	22.2	13.8	+2.4
Acetoacetic ester	13.5	12.8	9.6	−16.5
Benzoylacetone	18.3	17.7	13.8	+2.81
Acetophenone	11.4	10.8	5.9	−33.7
p-Chloroacetophenone	11.4	10.8	5.9	−33.2
p-Bromoacetophenone	13.1	12.4	7.2	−27.7
p-Nitroacetophenone	17.2	16.5	10.3	−13.7
p-Methylacetophenone	11.4	10.8	5.8	−34.2
m-Nitroacetophenone	16.4	15.7	9.6	−16.8
Cyclohexanone	15.3	14.6	9.7	−16.3
Cyclopentanone	16.9	16.3	10.1	−14.2
Cycloheptanone	14.6	13.9	8.3	−22.6
Cyclooctanone	14.3	13.6	8.7	−20.9

K₂SO₄ and MnSO₄ decreases the rate. Retardation by MnSO₄ is more significant in the case of cyclohexanone (Table 4).

Nature of the oxidizing species — If MnO_4^- is primarily responsible for the oxidation, the addition of Mn^{2+} should reduce [permanganate] and hence cause retardation, whereas acceleration should be observed if Mn(III) ions are the oxidizing species

$$MnO_4^- + 3Mn^{2+} + 8H^+ \longrightarrow 3Mn^{3+} + Mn^{4+} + 4H_2O$$
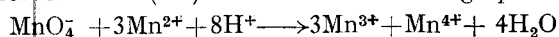
Similarly if MnO_4^- ion is the initial oxidizing species, the addition of fluoride ion will cause no appreciable change in the rate of oxidation. On the other hand, if Mn(III) or Mn(IV) ions are active oxidizing species a large retardation in the rate will be observed on the addition of sodium fluoride. In the present study available experimental data conclusively show that permanganate ion is the initial oxidizing species.

Effect of Temperature

The second order rate constants at 35°, 40° and 45° are given in Table 3. The values of various thermodynamic parameters calculated from the Arrhenius plot are given in Table 5. The plot of log A versus $1/\sqrt{E}$ is linear, as expected on the basis of thermodynamic considerations[14,15], if both the Arrhenius parameters control the reaction rate. Leffler and Grunwald[16] have pointed out that many reactions show isokinetic relationship given by $\Delta H\ddagger = C + \beta\Delta S\ddagger$.

A plot of $\Delta H\ddagger$ versus $\Delta S\ddagger$ is linear with the parameters $C = 20.5$ kcal mole⁻¹ and $\beta = 312.5°K$ for acetophenone series. Plot of $\Delta H\ddagger$ versus $\Delta S\ddagger$ is fairly linear for aliphatic ketones and cyclic ketones with parameters $C = 21$ kcal mole⁻¹, $\beta =$

500°K and $C = 18.6$ kcal mole⁻¹, $\beta = 208.3°K$ respectively. The β values obtained for each series of aliphatic ketones, aryl aliphatic ketones and cyclic ketones are significant and deserve comment. In general, one can say that the order of reactivity seems to parallel the isokinetic temperature of each series. The range of β values derives support from the fact that a similar relationship exists for the dielectric relation as well.

Mechanism — Radhakrishnamurti and Sushila Devi[1] ruled out the possibility of the mechanism postulated by Speakman and Waters[17] in the oxidation of aliphatic and aryl aliphatic ketones by hexacyanoferrate and preferred a mechanism postulated by Singh et al.[3]. With the data available it may be suggested here that the reactions proceed via enol form of the ketones and the oxidant is permanganate ion. The rate determining step involves a two-electron transfer from the enol resulting in oxonium ion mesomeric with the carbonium ion, which in a fast step gives the products. The reaction sequence may be represented as shown in Scheme 1.

Mn(V) ⟶ Mn(III) + Mn(II);

2Mn(III) ⟶ Mn(IV) + Mn(II)
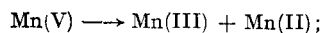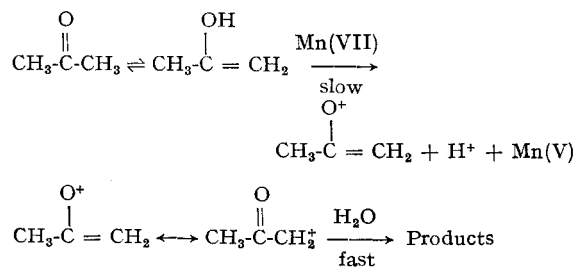
Scheme 1

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