February, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 61, 543—547 (1988)* 543

Kinetics of Oxidation of Aliphatic Ketones with Bromamine-T in Acid Medium

Dandinasivara Siddalingaiah MAHADEVAPPA* and Putta SWAMY
Department of Chemistry, University of Mysore, Manasagangothri, Mysore 570006, India
(Received September 26, 1986)

The kinetics of oxidation of 2-propanone, 2-butanone, 2-pentanone, 3-pentanone, and 4-methyl-2-pentanone by sodium salt of *N*-bromo-*p*-toluenesulfonamide or bromamine-T (BAT) in presence of $HClO_4$ was studied at 30 °C. The rate law is:

$$-\frac{d[BAT]}{dt}=k[BAT]^0[ketone]^1[H^+]^1.$$

Variation of ionic strength of medium or addition of reaction product *p*-toluenesulfonamide have no effect on the rate. The dielectric effect is positive. The acid-catalyzed enolization of ketone is assumed to be the rate-limiting step and enolization rate coefficients have been calculated. Proton inventory studies made in H_2O-D_2O mixtures have been employed to calculate the isotopic fractionation factors. Isokinetic temperature is 320 K indicating enthalpy as a controlling factor.

Although the analytical applications and kinetic studies of reactions of the organic chloramines, chloramine-T (CAT) and chloramine-B (CAB) are reviewed,[1] there is scant information in literature about the bromine analogues. As a part of our mechanistic studies of oxidation of substrates by *N*-bromo amides, we report the kinetics of oxidation of aliphatic ketones, 2-propanone, 2-butanone, 2-pentanone, 3-pentanone, and 4-methyl-2-pentanone by bromamine-T (p-$CH_3C_6H_4SO_2NBrNa \cdot 3H_2O$ or BAT) in presence of perchloric acid.

Experimental

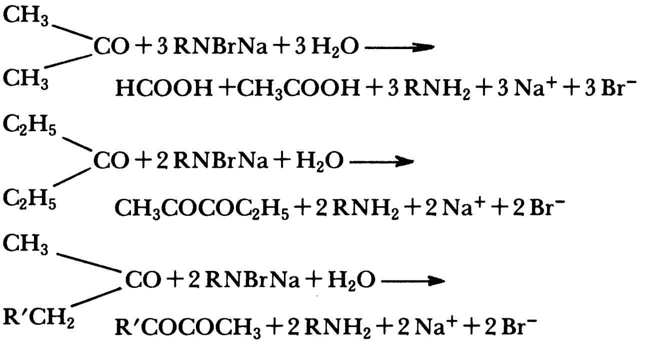
Bromamine-T was prepared by the method reported in literature.[2] The authenticity of the product was confirmed by checking iodometrically and then through its mass spectrum and UV, IR, ^1H, and ^{13}C-spectral data. An aqueous solution of BAT was prepared, standardized by the iodometric method and was preserved in brown bottles to prevent its photochemical deterioration.

Analytical grade acetone was used without further purification while other ketones (SDS, India) were redistilled. Aqueous solutions of ketones (≈0.2M) (1 M=1 mol dm^{-3}) were prepared by exact weighing of required quantity of the compound. All other chemicals were of analytical grade. Triply distilled water was used in preparing aqueous solutions.

Regression analysis of experimental data (to get regression coefficient *r* and standard deviation of the estimate, *S*) carried out on a TDC-316 (16 bits) computer supplied by Trombay Electronics, India.

Kinetic Measurements. Rate studies were made at 30 °C and details are described in some of the previous communications.[3] The course of reaction was studied for about three half-lives. The pseudo-zero-order rate constants obtained from the plots of $\{[BAT]_0-[BAT]\}$ versus time were converted into standard zero-order constants k_0 through the equation, $k_0=SN/V$ where S is the slope of the plot, N the normality of thiosulfate used for iodometric estimation of unreacted BAT and V is the aliquot of reaction mixture titrated. The pseudo-first-order rate constants k' were calculated by the relation, $k'=k_0/[\text{ketone}]$. The rate constants were reproducible to ±3%.

Stoichiometry. Studies on stoichiometry indicated that 2-propanone consumes 3 moles of BAT per mole of ketone corresponding to the formation of HCOOH and CH_3COOH. The ratio was 2 : 1 in the case of other ketones indicating the formation of diketones.



$$(CH_3)_2CO+3\,RNBrNa+3\,H_2O\longrightarrow HCOOH+CH_3COOH+3\,RNH_2+3\,Na^++3\,Br^-$$

$$(C_2H_5)_2CO+2\,RNBrNa+H_2O\longrightarrow CH_3COCOC_2H_5+2\,RNH_2+2\,Na^++2\,Br^-$$

$$CH_3COCH_2R'+2\,RNBrNa+H_2O\longrightarrow R'COCOCH_3+2\,RNH_2+2\,Na^++2\,Br^-$$

where R′=-CH_3 for 2-butanone, -CH_2CH_3 for 2-pentanone, -$CH(CH_3)CH_3$ for 4-methyl-2-pentanone and R= p-$CH_3C_6H_4SO_2$.

The sulfonamide (reduction product of BAT) was detected by paper chromatography.[3] Formic and acetic acids were identified through TLC followed by conventional spot test analysis and were estimated by titration with standard alkali (Table 1). The reaction mixture was extracted with ether and the diketones present were detected through TLC followed by spot tests. Biacetyl (bp 88—91 °C) formed had a bp of

Table 1. Estimation of the Products of Oxidation of 2-Propanone and 2-Butanone by BAT in Acid Medium

Amount of acid found/10^{-3} mol[a]		Amount of 2,4-DNP hydrazone formed/g[b]	
Theoretical	Found	Theoretical	Found
4.0	3.7	1.50	1.42
6.7	6.5	2.90	2.72
8.0	7.9	5.50	5.10
10.0	8.8	—	—
12.0	11.7	—	—
16.0	15.9	—	—
20.0	19.0	—	—

a) From the reaction of 2-propanone. b) From the reaction of 2-butanone.

90 °C (corrected) and was assayed as its 2,4-DNP derivative (Table 1).

Results

At constant excess ketone concentration (0.05 mol dm^{-3}) and [$HClO_4$]=0.1 mol dm^{-3}, plots of {[BAT]$_0$ −[BAT]} versus time were found to be linear ($r>0.9968$ $S<0.0184$) passing through the origin indicating zero-order dependence on [oxidant]. The pseudo-zero-order rate constants are found to be truly constant for different oxidant concentrations indicating that oxidation of substrate is complete (Table 2). The rate increased with [ketone]$_0$ and linear ($r>0.9979$, $S\leqq0.0120$) with unit slope (Table 3). Further, a plot of k_0 versus [ketone]$_0$ is linear ($r>0.9988$, $S\leqq0.0156$) passing through the origin confirming the first-order dependence on [substrate]$_0$ in each case. Increase in [$HClO_4$] increased the rate of reaction and a plot of log k_0 versus log[$HClO_4$] was linear ($r>0.9969$, $S\leqq0.0208$) with a slope of unity (Table 4) showing a first-order dependence on [H^+]. When k_0 versus [$HClO_4$] was plotted, it gave a straight line passing through the origin ($r>0.9980$, $S\leqq0.0234$) indicating that the reaction takes place only through the acid-dependent path. When ionic strength of solution was varied by adding $NaClO_4$, the rate was unaffected (Tables 1 and 2). Addition of reaction product, *p*-toluenesulfonamide (RNH_2) or Br^- ion had no influence on the rate. The solvent composition was varied by adding methanol to the reaction mixture (0—40% v/v). The rate increased with increase in methanol concentration and a plot of log k_0 versus D^{-1}, where D is the dielectric constant of medium gives a straight line ($r>0.9971$ $S\leqq0.0126$) with a positive slope. Blank experiments showed that

Table 2. Effect of [BAT]$_0$ and Ionic Strength Variation on the Rate of Oxidation of Ketone at 30 °C
[ketone]$_0$=0.05 mol dm^{-3}; [$HClO_4$]=0.10 mol dm^{-3}; μ=0.5 mol dm^{-3}

[BAT]$_0$	k_0/10^{-7} mol dm^{-3} s^{-1}				
10^{-4} mol dm^{-3}	2-Propanone	2-Butanone	2-Pentanone	3-Pentanone	4-Methyl-2-pentanone
6.0	5.08	6.20	5.87	5.80	6.93
7.0	5.07	6.25	5.78	5.67	7.00
8.0	4.80	6.00	5.81	5.83	6.80
9.0	5.00	6.11	5.83	5.75	6.78
10.0	4.75	6.08	5.83	5.67	6.67
11.0	5.00	6.00	5.92	5.81	6.75
9.0[a]	5.00	6.00	5.80	5.67	6.83
9.0[b]	4.85	6.08	5.75	5.75	6.93
9.0[c]	5.00	6.11	5.83	5.75	6.78
9.0[d]	4.87	6.22	5.92	5.92	6.67

At ionic strength (μ)=0.20, a) 0.30, b) 0.50, c) and 0.80, d) mol dm^{-3}.

Table 3. Variation of [ketone] on the Reaction Rate at 30 °C.
[BAT]$_0$=9.0×10^{-4} mol dm^{-3}; [$HClO_4$]=0.10 mol dm^{-3}; μ=0.5 mol dm^{-3}

[ketone]$_0$	k_0/10^{-7} mol dm^{-3} s^{-1}				
10^{-2} mol dm^{-3}	2-Propanone	2-Butanone	2-Pentanone	3-Pentanone	4-Methyl-2-pentanone
3.0	3.00	3.60	3.44	3.39	4.07
4.0	3.94	4.53	4.80	4.44	5.33
5.0	5.00	6.11	5.83	5.75	6.78
6.0	5.93	7.33	7.00	7.02	8.00
7.0	6.89	8.56	8.50	8.11	9.67
9.0	9.11	10.91	10.33	10.13	12.17

Table 4. Variation of [$HClO_4$] on the Reaction Rate at 30 °C
[BAT]$_0$=9.0×10^{-4} mol dm^{-3}; [ketone]=0.05 mol dm^{-3}; μ=0.5 mol dm^{-3}

[$HClO_4$]$_0$	k_0/10^{-7} mol dm^{-3} s^{-1}				
10^{-2} mol dm^{-3}	2-Propanone	2-Butanone	2-Pentanone	3-Pentanone	4-Methyl-2-pentanone
6.0	2.78	3.83	3.50	3.33	4.17
8.0	4.00	5.00	5.04	4.60	5.42
10.0	5.00	6.11	5.83	5.75	6.78
12.0	5.80	7.67	7.11	6.50	8.40
14.0	6.67	9.17	8.33	8.11	9.83
16.0	8.00	9.83	9.50	9.00	10.83

Table 5. Kinetic and Thermodynamic Parameters for the Oxidation of Ketone by BAT in Perchloric Acid Medium

Ketone	E_a/kJ mol^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1}mol^{-1}	$\Delta G^{\neq}$/kJ mol^{-1}	log A
2-Propanone	77.1	74.6	−94.8	103.3	9.3
2-Butanone	71.3	68.7	−112.3	102.8	8.4
2-Pentanone	74.3	71.7	−102.7	102.9	8.9
3-Pentanone	78.3	75.8	−89.3	102.9	9.6
4-Methyl-2-pentanone	69.6	67.1	−117.2	102.6	8.1

Table 6. Proton Inventory Studies for 2-Propanone in H_2O-D_2O Mixture at 30 °C. $[\mathrm{BAT}]_0=9.0\times10^{-4}$ mol dm^{-3}, [ketone]$=0.05$ mol dm^{-3}; $[\mathrm{HClO_4}]=0.10$ mol dm^{-3}; $\mu=0.5$ mol dm^{-3}

Atom fraction of deuterium (n)	$k_0^n/10^{-7}$ mol dm^{-3} s^{-1}
0.00	5.08
0.248	5.75
0.496	6.67
0.744	7.52
0.992	8.57

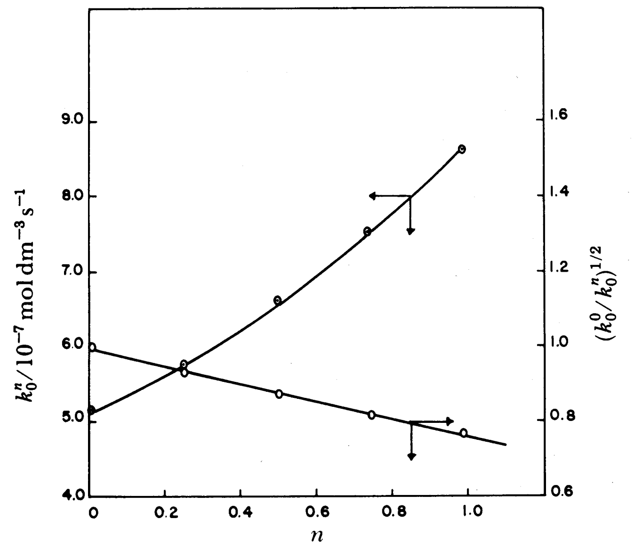


Fig. 1. Proton inventory plot for the oxidation of 2-propanone by BAT in H_2O-D_2O mixtures at 30 °C. $[\mathrm{BAT}]_0=9.0\times10^{-4}$ mol dm^{-3}; $[\mathrm{ketone}]_0=0.05$ mol dm^{-3}; $[\mathrm{HClO_4}]=0.1$ mol dm^{-3}.

methanol is not oxidized by BAT under the present experimental conditions.

Addition of reaction mixture to aqueous acrylamide did not initiate polymerization showing absence of free radicals.

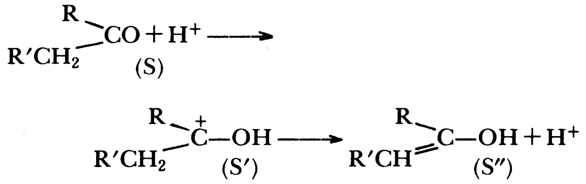
The reaction was studied at different temperatures (293—313 K) and from the Arrhenius plots of log k' versus T^{-1} ($r>0.9985$, $S\leq0.037$) the kinetic parameters were calculated (Table 5).

Solvent isotope studies were made in D_2O medium. For 2-propanone value of k_0 in D_2O was 8.57×10^{-7} mol dm^{-3} s^{-1} while the corresponding value in H_2O was 5.08×10^{-7} mol dm^{-3} s^{-1} leading to a solvent isotope effect $(k_0)_{H_2O}/(k_0)_{D_2O}=0.59$ with other conditions as in Table 2. Proton inventory studies with 2-propanone as the probe were made in H_2O-D_2O mixtures and these results are shown in Table 6. The corresponding proton inventory plot relating to the rate constant k_0^n in a solvent mixture of deuterium atom fraction n is given in Fig. 1.

Discussion

Bromamine-T is analogous[5] to chloramine-T and chloramine-B and with the assumption of similar equilibria in acidified aqueous solutions of oxidant, the possible oxidizing species in these solutions are RNHBr, $RNBr_2$, and HOBr where R=p-$CH_3C_6H_4SO_2$. But the zero-order dependence on [oxidant] precludes speculation about the identity of kinetically active species. It is likely that the free acid RNHBr which is in higher concentrations[5] compared to the other species would oxidize the ketones in a fast step.

Ketones form oxonium salts on protonation in presence of strong acids leading to enolization:



$$\underset{\text{(S)}}{\mathrm{R(R'CH_2)CO}} + \mathrm{H^+} \longrightarrow \underset{\text{(S')}}{\mathrm{R(R'CH_2)\overset{+}{C}{-}OH}} \longrightarrow \underset{\text{(S'')}}{\mathrm{R(R'CH){=}C{-}OH}} + \mathrm{H^+} \qquad (1)$$

Here S represents the ketone, S′ its conjugate acid and S″ its enolic form.

The first-order dependence of rate on [ketone] and [H$^+$] and the zero-order in $[\mathrm{BAT}]_0$ shows that the traditional mechanism of Bell and co-workers[6] is followed (Scheme 1):

$$\mathrm{S+H^+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S' \text{ (fast)} \qquad \text{(i)}$$

$$\mathrm{S'} \xrightarrow{k_2} \mathrm{S''+H^+} \text{ (slow and r.l.s.)} \qquad \text{(ii)}$$

$$\mathrm{S''} + n\,\mathrm{RNBrNa} \xrightarrow{k_3} n\,\mathrm{RNH_2} + \text{Products (fast)} \qquad \text{(iii)}$$

Scheme 1.

Here $n=3$ for 2-propanone and 2 for other ketones.

Scheme 1 leads to rate law (2) which is in agreement with the observed stoichiometry and kinetic orders:

$$-\frac{\mathrm{d[BAT]}}{\mathrm{d}t}=\frac{2k_1k_2}{k_{-1}+k_2}[\text{ketone}][\text{H}^+] \qquad (2)$$

The positive dielectric effect indicates a charge dispersal in transition state pointing towards an ion-dipole reaction and is also in general agreement about its influence[7] on keto-enol equilibria.

The proposed mechanism is also supported by the magnitude of solvent isotope effect. The rate is enhanced in D_2O medium implying preequilibrium fast proton transfer with specific acid catalysis. It is well-known[8] that D_3O^+ is a stronger acid than the hydronium ion and hence a rate enhancement in D_2O should be expected. This is in agreement with the carbonium ion character of the transition state (Eq. 1) and lends support to the participation of enol form in the rate-limiting step. The proton inventory plot (Fig. 1) could throw light on the nature of transition state.[9,10] The dependence of rate constant k_0^n on n, the atom fraction of deuterium in a solvent mixture containing H_2O and D_2O is given by Eq. 3:

$$\frac{k_0^n}{k_0^0}=\frac{\prod\limits^{\mathrm{TS}}(1-n+n\phi_i)}{\prod\limits^{\mathrm{RS}}_{\mathrm{J}}(1-n+n\phi_{\mathrm{J}})} \qquad (3)$$

Here ϕ_i and ϕ_J are isotopic fractionation factors for isotopically exchangeable hydrogenic sites in the transition state (TS) and reactant site (RS) respectively. If it is assumed that the reaction proceeds through a single transition state, Eq. 3 takes the forms shown by Eqs. 4 and 5:

$$k_0^n=k_0^0(1-n+n\phi_{\mathrm{J}})^{-2} \qquad (4)$$

$$\left(\frac{k_0^0}{k_0^n}\right)^{1/2}=[1+n(\phi_{\mathrm{J}}-1)] \qquad (5)$$

Equation 5 indicates a linear relation between $(k_0^0/k_0^n)^{1/2}$ and n and this is shown in Fig. 1 (r=0.9988, S=0.0391). The slope (ϕ_J-1)=−0.24, from which the fractionation factor is found to be 0.76. Kresge and Allred[11] have obtained a value of 0.67 for the fractionation constants of $HClO_4$ in H_2O-D_2O mixtures, while Gold[12] reported a value of 0.69±0.02. Considering the diversity of procedures employed, it may be assumed that there is agreement between the values and the fractionation factor refers to $HClO_4$. Exchange of ketone with D_2O was also checked for a primary isotope effect but this was found to be negligible for the duration of experiment. However, a trial experiment with ordinary acetone equilibrated in 60% D_2O over a period of 48 h showed that $k_0=2.51\times10^{-7}$ mol l^{-1} s^{-1} while the corresponding blank value (zero time) was 5.18×10^{-7} mol l^{-1} s^{-1} giving $k_H/k_D=2.1$. Reitz[13] has shown that acetone-d_6 reacts 7.7 times slower than ordinary acetone under identical conditions. It may therefore be inferred that exchange to an extent of about 27% has occurred in 48 h.

The reaction is characterized by a moderate energy of activation. The large negative $\Delta S^{\neq}$ values point towards a rigid transition state. Satisfactory structure-reactivity correlations cannot be drawn in the present studies due to the zero-order observed in [oxidant]$_0$. Values of the first-order rate constant $k'=k_0/[\text{ketone}]$ for the different ketones are almost the same indicating the absence of significant effects of structure on the enolization of ketones (Table 7). The enolization coefficients, $k''=k_s/[\text{ketone}][\text{H}^+]$ are shown in Table 7. The values for 2-propanone and 3-pentanone are 10.0×10^{-5} and 11.5×10^{-5} dm^3 mol^{-1} s^{-1} at 30 °C which are comparable with those obtained by Toullec and Dubois[14] in H_2SO_4 at 25 °C.

Table 5 shows that the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ decrease in the order:

4-methyl-2-pentanone < 2-butanone
< 2-pentanone < 2-propanone < 3-pentanone

An isokinetic relationship can be envisaged since a plot of $\Delta H^{\neq}$ versus $-\Delta S^{\neq}$ is linear (r=0.9983, S=0.24). From the slope, the value of isokinetic temperature β is 320 K. The relationship was tested through the Exner criterion[15] by plotting log k_{30} versus log k_{20} and was found to be genuine. From this plot, β was found to be 350 K. The value of β is slightly higher than the experimental temperature (303 K) indicating enthalpy as a controlling factor. Current views[16] do not attach much significance to the concept of isokinetic temperature, as the Exner criterion is a necessary follow up factor of the isokinetic relation. The constancy of $\Delta G^{\neq}$ values however indicates that a similar mechanism is operative in the oxidation of ketones by BAT.

It is noted in the present studies that a zero-order

Table 7. Enolization Coefficients Observed during the Oxidation of Aliphatic Ketones by BAT at Different Temperatures in Presence of 0.1 M $HClO_4$

Ketone	$k'/10^{-6}$ s^{-1}					$k''/10^{-5}$ dm^3 mol^{-2} s^{-1}				
	293	298	303	308	313	293	298	303	308	313
2-Propanone	3.80	5.34	10.00	16.00	28.00	3.80	5.34	10.00	16.00	28.00
2-Butanone	4.66	6.94	12.22	20.26	32.00	4.66	6.94	12.22	20.26	32.00
2-Pentanone	4.38	7.06	11.66	18.00	32.00	4.38	7.06	11.66	18.00	32.00
3-Pentanone	4.26	6.94	11.50	20.00	33.34	4.26	6.94	11.50	20.00	33.34
4-Methyl-2-pentanone	5.34	8.34	13.56	19.66	34.66	5.34	8.34	13.56	19.66	34.66

dependence on $[\mathrm{BAT}]_0$ indicates the operation of the traditional mechanism of Bell and co-workers[6] with enolization as rate-limiting step, while with the chlorine analogue, addition of halogen derivative takes place in the rate determining stage. A similar observation is made in the oxidation of dimethyl sulfoxide by the chloramines[17] and bromamines,[18] which probably is a reflection on the relative electrophilicity of the halonium cations, Cl^+ and Br^+ of the compounds, which are involved in the reaction sequence.

One of us (PS) gratefully acknowledges the award of a Post-graduate Research Fellowship to him from the University of Mysore. The authors thank the referees for valuable suggestions.

References

1) M. M. Campbell and G. Johnson, *Chem. Rev.*, **78**, 65 (1978); K. K. Banerji, B. Jayaram, and D. S. Mahadevappa, *J. Sci. Ind. Res.*, in press; B. T. Gowda and D. S. Mahadevappa, *J. Chem. Soc., Perkin Trans 2*, **1983**, 323.

2) C. G. R. Nair, R. Lalithakumari, and P. I. Senan, *Talanta*, **25**, 525 (1978).

3) D. S. Mahadevappa, S. Ananda, M. B. M. Bowda, and K. S. Rangappa, *J. Indian Chem. Soc.*, **61**, 323 (1984); *Indian J. Chem.*, **23A**, 325 (1984); D. S. Mahadevappa and K. Mohan, *Oxidation Comm.*, **8**, 207 (1985/86); *Tetrahedron*, **42**, 4857 (1986).

4) F. Feigl, "Spot Tests in Organic Analysis," Elsevier, Amsterdam (1956), pp. 205, 340.

5) E. Bishop and V. J. Jennings, *Talanta*, **1**, 197 (1958).

6) R. P. Bell and G. Archer, *J. Chem. Soc.*, **1959**, 3228; R. P. Bell and K. Yates, *ibid.*, **1962**, 1927.

7) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York (1964), p. 380.

8) "Isotope Effect in Chemical Reactions," ed by C. J. Collins and N. S. Bowman, Van-Nostrand-Reinhold, New York (1970), p. 267.

9) W. J. Albery and M. H. Davies, *J. Chem. Soc., Faraday Trans.*, **68**, 167 (1972).

10) G. Gopalakrishnan and J. L. Hogg, *J. Org. Chem.*, **50**, 1206 (1985).

11) A. J. Kresge and A. L. Allred, *J. Am. Chem. Soc.*, **85**, 1541 (1963).

12) V. Gold, *Proc. Chem. Soc. (London)*, **1963**, 141.

13) O. Reitz, *Z. Phys. Chem.*, **A179**, 119 (1937).

14) J. Toullec and J. E. Dubois, *Tetrahedron*, **29**, 2851, 2859 (1973).

15) O. Exner, *Collect. Czech. Chem. Commun.*, **29**, 1094 (1964).

16) J. E. Leffler, *J. Org. Chem.*, **31**, 533 (1966).

17) D. S. Mahadevappa, M. B. Jadhav, and H. M. K. Naidu, *Int. J. Chem. Kinet.*, **11**, 261 (1979).

18) D. S. Mahadevappa, S. Ananda, A. S. A. Murthy, and K. S. Rangappa, *Tetrahedron*, **40**, 1673 (1984).