KINETICS OF HYDROLYSIS OF 1,3,5-TRIAZINE IN MILDLY ACIDIC MEDIA

Marina Privman and **Petr Zuman***

Department of Chemistry, Clarkson University
Potsdam, NY 13699-5810, USA

Abstract - Acid catalyzed hydrolysis of 1,3,5-triazine at pH 2 to 5 is governed by the rate of the ring opening. This follows from the value of the dissociation constant involved (pK_a 2.7 at $\mu = 0.5$ and pK_a 2.3 at $\mu = 0.1$), from the lack of pH-dependence of concentration of 1,3,5-triazine at $t = 0$, and from the irreversibility of the studied reaction.

INTRODUCTION

Derivatives of 1,3,5-triazines are important as pesticides,[1-5] are used in manufacture of dyes, and in modification of electrode surfaces. Their interaction with proteins (such as photographic gelatin) and cellulosics also find industrial applications.[6-13] Because of the importance of substituted triazines as pesticides and their possible degradation,[1-4] attention has been paid to the substitution of halogens in halogen derivatives of 1,3,5-triazines by hydroxides[2,3,5] or alkoxides, as well as to their acid catalyzed hydrolysis.[4,5] Some of the reactions in the presence of cyanuric chloride (2,4,6-trichloro-1,3,5-triazine), e.g., binding to cellulosics[6-9] or hardening of photographic emulsions[10-13] occur in alkaline media and actually involve its hydrolysis products. Therefore, the base catalyzed hydrolysis of cyanuric chloride, which involves a nucleophilic substitution of one chlorine atom by a hydroxide ion in the first step, has been investigated in some detail.[7,8,14-16] The rate of competitive protonation of the adduct[15] was questioned.[7] Alternatively, the nucleophilic substitution of chlorine can occur in a reaction with water[17-20] or alkoxide ions.[21]

Only qualitative information is available[22-25] concerning the solvolysis of the 1,3,5-unsubstituted triazine. In aqueous solutions the hydrolysis occurs at 25°C in a matter of minutes. Changes with time occur also in alcoholic solutions as well as solutions in dimethylformamide.[23] Acidic catalysis of hydrolysis was indicated,[23] but no kinetic data that might contribute to the elucidation of the mechanism of processes involved were reported. In the course of investigation of the polarographic reduction of 1,3,5-triazines[26] some understanding of kinetics of hydrolysis became essential. Results of our kinetic studies are presented in the present paper together with an attempt to propose the mechanism of the studied reaction. Both spectrophotometry and polarography were used to follow changes in concentration of 1,3,5-triazine with time.

EXPERIMENTAL

Instrumentation. Uv absorption spectra were recorded with Perkin-Elmer Mark 559 spectrophotometer at 25°C. Dc polarographic curves were obtained with IBM Instruments Inc. EC/225 Voltammetric Analyzer and 7424MT X-Y-T recorder at 25°C and 0°C. pH measurements were carried out with Radiometer Copenhagen PHM 84 Research pH Meter, equipped with Radiometer G202B glass and K422 (saturated KCl) calomel electrodes.

Polarographic work was conducted in a Kalousek cell using liquid junction separated SCE as a reference electrode. For measurements at 0°C the cell was immersed in an ice bath and adequate time for thermal equilibration was allowed for before measurement. The dropping mercury electrode was a Smoler capillary with an orifice bent by 90°. The capillary had $m = 0.64\,\mathrm{mg/s}$ and $t = 1.8\,\mathrm{s}$ at $h = 72\,\mathrm{cm}$ in 0.1 M KCl at 0.0 V *vs.* SCE.

Chemicals and Solutions. 1,3,5-Triazine was supplied by Aldrich, contained 97% of the active species and was used without further purification. Chemicals for preparation of buffers and supporting electrolytes were reagent or analytical grade. A 0.01 M stock solution of 1,3,5-triazine in acetonitrile was prepared fresh every three days.

The composition of buffers used for polarographic measurements was: for pH 5.7 to 3.4 acetate buffers, for pH 4.8 to 2.8 formate buffers, and for pH 1.7 to 3.0 phosphate buffers (H_3PO_4/NaH_2PO_4). These were prepared in such a way that the final concentration of the anion was 0.5 M and the concentration of the corresponding acid varied ($\mu = 0.5$). Spectrophotometric measurements were carried out in formate buffers pH 4.8 to 2.8 containing 0.1 M formate ($\mu = 0.1$).

Procedures. For polarography, addition of 0.1 ml of 0.01 M 1,3,5-triazine to 10 ml of the buffer used was immediately followed by introduction of nitrogen. After 2.5-3 min of purging the first current-voltage curve was recorded. This was followed by successive curves recorded in 30 s to 180 s intervals. In the pH range from 1.6 to 5.8 polarographic reduction of 1,3,5-triazine occurs in up to three waves. The interpretation of the electrode process will be published elsewhere.[26] For kinetic studies only the limiting current of the first wave was measured and current-voltage curves were recorded in the potential region in which this wave appeared. The current was shown to be a linear function of concentration of triazine in the $5 \cdot 10^{-5}$ M to $2 \cdot 10^{-4}$ M concentration range.

For spectrophotometry, 2 ml of the buffer was placed into the optical cell, 40 to 80 μl of 0.01 M

1,3,5-triazine added and the solution homogenized by shaking. The first spectrum was recorded 30 s after addition of triazine and subsequent spectra were recorded in 60 s intervals. Absorbance at 260 nm was measured and used for kinetic studies.

RESULTS

The concentration of 1,3,5-triazine, as followed *in situ* by spectrophotometry and polarography, changes with time. At pH 2 to 5 the rate of this change, attributed to hydrolysis, increases with the acidity of the reaction mixture. At pH 6 to 10 solvent and base catalyzed hydrolysis predominates. At 25°C the rate of hydrolysis for $\mathrm{pH} < 2.5$ becomes too fast to be measured by the techniques used. In strongly acidic solutions, 96% H_2SO_4, Korolev *et al.*[27] observed time-independent spectra, which they attributed to a monoprotonated hydrated form of triazine. Actually, the situation is more complex, with a sequence of several gradually more protonated species formed with increasing acidity. These species differ in the wavelengths of their absorption maxima and some of them undergo hydrolysis. Reactions at $\mathrm{pH} > 6$ are currently under investigation. In this contribution we shall restrict ourselves to a discussion of the acid-catalyzed hydrolysis at pH 2 to 5, where the reaction has been proved to be irreversible.

Both the polarographic limiting current of 1,3,5-triazine (i_1) and its absorbance (A) at 260 nm are a linear function of concentration and, hence, can be directly used in an evaluation of rate constants from the rate equation. Replacing both measured quantities (i and A) by a general symbol ϕ, it was first proved that the reaction follows strictly the first order kinetics by plotting $\ln\phi = f(t)$. Resulting plots were strictly linear at least up to 75% conversion. Using the expression (1):

$$\ln\phi = -k't + \ln\phi_0 \quad , \tag{1}$$

the slopes of such plots yielded values of k' at each pH value. Values obtained with spectrophotometry were in good agreement with those obtained by polarography, as shown in Table 1 and Figure 1. Values of the rate constant k' increase with increasing acidity (Table 1), indicating a presence of an acid-base equilibrium rapidly established before the rate determining step in which the conjugate acid form participates: $AH^+ \rightleftharpoons A + H^+$; $AH^+ + R \rightarrow P$. For such system the dependence of the measured rate constant k' on activity of H^+ can be expressed[28] by (2):

$$k' = \frac{k[H^+]}{K_a + [H^+]} \quad , \tag{2}$$

with two unknown quantities, k (the hydrolysis rate constant) and K_a (the acid dissociation constant). Unavailability of data at $\mathrm{pH} < 2.5$ prevented the direct measurement of the value of rate constant k as

Table 1. Experimental Values of the Rate Constant k' of Hydrolysis of 1,3,5-Triazine as a Function of pH.

Spectrophotometric Data		Polarographic Data		Polarographic Data	
$T = 25°\mathrm{C}$, $\mu = 0.1$		$T = 25°\mathrm{C}$, $\mu = 0.5$		$T = 0°\mathrm{C}$, $\mu = 0.5$	
pH	k'/s^{-1}	pH	k'/s^{-1}	pH	k'/s^{-1}
4.86^a	$1.3 \cdot 10^{-4}$	5.28^b	$7.7 \cdot 10^{-5}$	4.25^a	$9.0 \cdot 10^{-5}$
4.65^a	$3.4 \cdot 10^{-4}$	5.08^b	$1.8 \cdot 10^{-4}$	4.17^b	$1.3 \cdot 10^{-4}$
4.39^a	$5.8 \cdot 10^{-4}$	4.85^b	$2.0 \cdot 10^{-4}$	3.94^a	$2.3 \cdot 10^{-4}$
4.24^a	$7.4 \cdot 10^{-4}$	4.70^b	$3.2 \cdot 10^{-4}$	3.73^a	$3.4 \cdot 10^{-4}$
4.00^a	$1.2 \cdot 10^{-3}$	4.51^b	$5.1 \cdot 10^{-4}$	3.53^b	$6.1 \cdot 10^{-4}$
3.79^a	$2.3 \cdot 10^{-3}$	4.31^a	$6.7 \cdot 10^{-4}$	3.36^a	$8.6 \cdot 10^{-4}$
3.60^a	$2.9 \cdot 10^{-3}$	4.31^b	$7.3 \cdot 10^{-4}$	3.10^c	$1.7 \cdot 10^{-3}$
3.42^a	$4.6 \cdot 10^{-3}$	4.16^a	$9.7 \cdot 10^{-4}$	2.93^c	$3.7 \cdot 10^{-3}$
3.19^a	$7.3 \cdot 10^{-3}$	4.01^a	$1.3 \cdot 10^{-3}$	2.70^c	$5.2 \cdot 10^{-3}$
2.99^a	$1.1 \cdot 10^{-2}$	3.79^a	$2.0 \cdot 10^{-3}$	2.50^c	$1.1 \cdot 10^{-2}$
		3.59^a	$3.2 \cdot 10^{-3}$	2.33^c	$1.5 \cdot 10^{-2}$
		3.42^a	$4.5 \cdot 10^{-3}$	2.10^c	$2.3 \cdot 10^{-2}$

[a]Formate buffers: [b]Acetate buffers: [c]Phosphate buffers

well as an estimate of the pK_a value of the acid-base equilibrium involved. To estimate values of pK_a and k in (2), several trial values of K_a ranging from order 10^{-3} to order 10^0 were selected. For each K_a, the measured values of k' were considered as a function of $x = [\mathrm{H}^+]/\left(K_a + [\mathrm{H}^+]\right)$. These data were fitted to a straight line passing through the origin. The slope of this line obtained by least square fit is denoted as k_{fitted}. Thus, $k' = k_{\text{fitted}}\, [\mathrm{H}^+]/\left(K_a + [\mathrm{H}^+]\right)$. The quality of the fit for each selected value of K_a was measured by variance, defined by (3):

$$\Delta(K_a) = \sum_{(k',x)-\text{values}} \frac{\left(k' - k_{\text{fitted}}x\right)^2}{\left(k'\right)^2} \quad . \tag{3}$$

The best K_a range was located by the minimum of the variance $\Delta(K_a)$. The best values of the dissociation constant K_a and the rate constant k (equal to k_{fitted} at chosen K_a) for the three sets of experimental data are given in Table 2.

The variance changes little from its value at the minimum when K_a is varied, suggesting a large relative error in K_a which for various data sets was of the order of 30 to 50%. The quality of the fit is demonstrated

Table 2. The Best Values of Dissociation Constant K_a and Rate Constant k for the Acid Catalyzed Hydrolysis of 1,3,5-Triazine (T-temperature, μ-ionic strength).

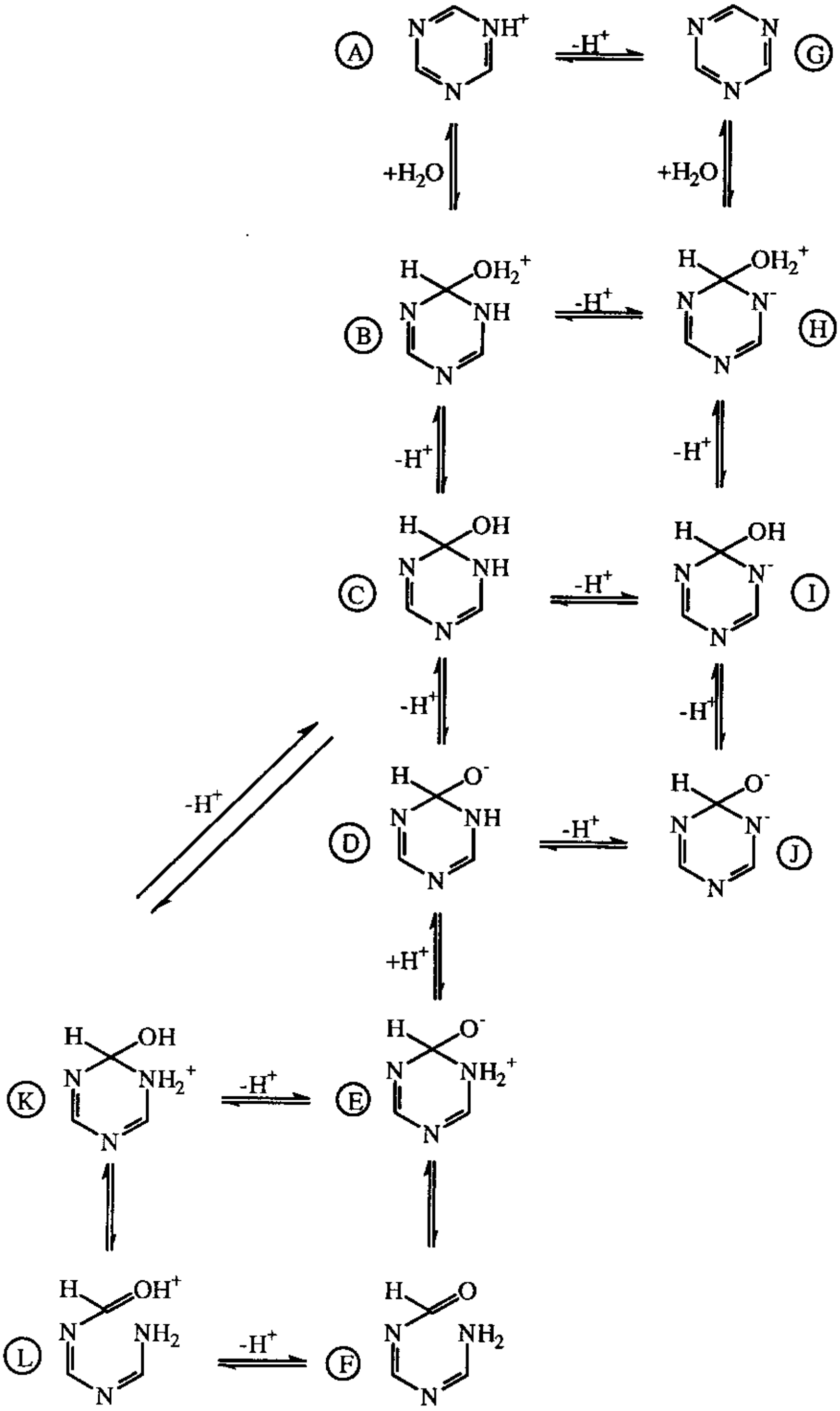
Set		Best Value	Technique	T	μ
1	K_a	0.0050 ± 0.0015	spectrophotometry	25°C	0.1
	k	$(6.5 \pm 1.7) \cdot 10^{-2}$			
2	K_a	0.0018 ± 0.0007	polarography	25°C	0.5
	k	$(2.5 \pm 0.9) \cdot 10^{-2}$			
3	K_a	0.07 ± 0.03	polarography	0°C	0.5
	k	$(1.7 \pm 0.9) \cdot 10^{-1}$			

for spectrophotometric (Figure 1a) and polarographic (Figure 1b) data obtained at 25°C with ionic strength $\mu = 0.1$ in the former and $\mu = 0.5$ in the latter case.

DISCUSSION

Experimental evidence indicates that in the pH range 2 to 5, 1,3,5-triazine undergoes hydrolysis in which the rate determining step is preceded by a rapidly established acid-base equilibrium (as indicated by the pH-dependence of the rate constant fitting (2)) and where the conjugate acid is the reactive species. The behavior of 1,3,5-triazine in this mildly acidic range can be described by Scheme 1. The majority of reactions in this Scheme are acid-base reactions involving *O*- or *N*-acids which can be considered under conditions used as rapidly established. Bond forming or bond braking reactions involving the conjugate acid are reactions $A \rightleftharpoons B$, $E \rightleftharpoons F$, and $K \rightleftharpoons L$. For reaction $A \rightleftharpoons B$ the antecedent protonation is $G + H^+ \rightleftharpoons A$, for reaction $E \rightleftharpoons F$ it is the protonation $D + H^+ \rightleftharpoons E$, and for reaction $K \rightleftharpoons L$ either $E + H^+ \rightleftharpoons K$ or $C + H^+ \rightleftharpoons K$.

The acid-base reaction preceding the rate determining step has a pK_a value about 2.5, as obtained by curve-fitting from the dependence of the rate constant k' on pH (Figure 1). This can not be reaction $A \rightleftharpoons G + H^+$, as over the pH range from 2 to 5 the absorbance at 260 nm or limiting current extrapolated to time zero remains unchanged. Furthermore, the wave-length of the absorption maximum also remains unchanged over the same pH range and the reaction is irreversible, as proved after pH increase of the reaction mixture. There are no reliable experimental data for the pK_a value for the dissociation of the monoprotonated form of 1,3,5-triazine, as the instability of aqueous solutions of this compound prevented its determination using potentiometric or conventional spectrophotometic techniques.[29] Potentiometric



Scheme 1

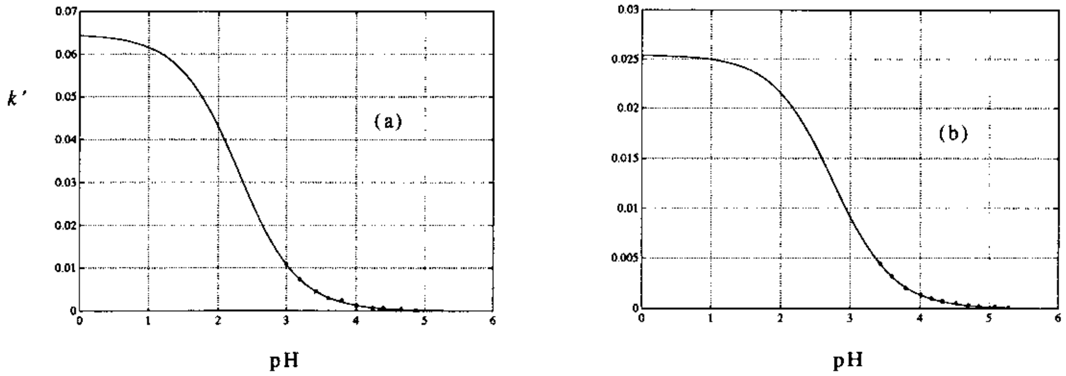


Figure 1. Dependence of the observed rate constant k' on pH at 25°C for hydrolysis of 1,3,5-triazine. (a) *Reaction followed spectrophotometrically,* $\mu = 0.1$, (b) *Reaction followed polarographically,* $\mu = 0.5$. *Theoretical curve calculated using equation (2) for:* (a) $K_a = 0.0050\,mol^{-1}$ *and* $k = 6.5 \cdot 10^{-2}\,s^{-1}$; (b) $K_a = 0.002\,mol^{-1}$ *and* $k = 2.5 \cdot 10^{-2}\,s^{-1}$ *and experimental points are shown.*

titration in nitromethane yielded for 1,3,5-triazine value pK_a (CH_3NO_2) 3.5 ± 0.2, from which it was possible to estimate the value in aqueous solutions pK_a (H_2O) -1.7, using a LFER, successfully applied to prediction of pK_a values of other azabenzenoid compounds.[30] Similarly, correlations with average local ionization energies calculated a SFC-MO theory yielded[31] a value for pK_a (H_2O) -2.3. Our preliminary measurements of spectra in sulfuric acid solutions also indicated for dissociation $A \rightleftharpoons G + H^+$ a constant pK_a (H_2O) about -2. Hence, when the pH is varied from 5 to 2, the dissociation of the protonated form of 1,3,5-triazine is not the acid-base process increasing the rate of hydrolysis, and the hydration of the protonated form $A + H_2O \rightleftharpoons B$ is not the rate determining step. This is further confirmed by the lack of pH-dependence of the absorbance at $t = 0$ and by the overall irreversibility of the studied process.

This leads to the conclusion that the ring opening is the rate determining step and the formation of the precursor in reactions $C + H^+ \rightleftharpoons K$ or $D + H^+ \rightleftharpoons E$ is a reaction with pK_a about 2.5. As acid catalyzed addition of amino group to a carbonyl group can occur in some instances in an attack on a protonated carbonyl group, ring opening $K \rightleftharpoons L$ seems more probable than $E \rightleftharpoons F$ and a proposed sequence involves a hydration of triazine $G + H_2O \rightleftharpoons H$ followed by several acid-base equilibria yielding K.

ACKNOWLEDGMENT

We express our gratitude to the U.S. Department of Agriculture, Forestry Service, for their support.

REFERENCES

1. D.D. Kaufman and P.C. Kearney, *Residue Rev.*, 1970, **32**, 235.
2. L. Różański, *Wiadom. Chem.*, 1987, **41**, 55.
3. L.E. Erickson and K.H. Lee, *Crit. Rev. Environ. Control*, 1989, **19**, 1.
4. D.E. Armstrong, G. Chester, and R.F. Harris, *Soil Sci. Soc. Amer. Proc.*, 1967, **31**, 61.
5. A. Velniceriu, L. Gavăt, and L. Tincu, *Rev. Chim.*, 1962, **13**, 513 (*Chem. Abstr.*, 1963, **59**, 5000e).
6. H. Ackermann and P. Dussy, *Helv. Chim. Acta*, 1962, **45**, 1683.
7. G.G. Allan, J.E. Killingbeck, and S.C. Roberts, *Paperi ja Puu*, 1974, **11**, 945.
8. R.Z. Shakirov, O.V. Gracheva, L.G. Fedorina, G.P. Krupnov, and R.A. Nurulina, *U.S.S.R. SU 1051082* (*Chem. Abstr.*, 1984, **100**, 94472p).
9. H.H. Sumner, *J. Soc. Dyers & Colour.*, 1960, **75**, 672.
10. L.T. Hodgins and M. Levy, *J. Chromatogr.*, 1980, **202**, 381.
11. J. Arient, J. Dostál, and J. Chludil, *Czech. CS 223478* (*Chem. Abstr.*, 1985, **102**, 36640x).
12. J. Arient, J. Dostál, and J. Chludil, *Czech. CS 224682* (*Chem. Abstr.*, 1985, **103**, 150889f).
13. D. Chen and B. Peng, *Ganguang Kexue Yu Kuang Huaxue*, 1985, **4**, 57.
14. S. Horrobin, *J. Chem. Soc.*, 1963, 4130.
15. P. Rys, A. Schmitz, and H. Zollinger, *Helv. Chim. Acta*, 1971, **54**, 163.
16. V.A. Marchukov, O.A. Nikitin, K.A. V'yunov, and A.I. Ginak, *Zh. Org. Khim.*, 1983, **19**, 2198.
17. L.A. Larionova, A.B. Koshokov, K.A. V'yunov, A.I. Ginak, and I. Krauklis, *Zh. Prikl. Khim. (Leningrad)*, 1982, **55**, 233 (*Chem. Abstr.*, 1982, **96**, 121940x).
18. R. Bacaloglu and J. Havlik, *J. Prakt.* Chemic., 1983, **325**, 309.
19. V.A. Korolev and M.A. Mal'tseva, *Zh. Org. Khim.*, 1975, **11**, 2613.
20. K.J. Bienkiewicz and L. Orszulski, *Rev. Tech. Ind. Cuir.*, 1980, **72**, 165.
21. L. Legradi and J. Huszar, *Magy. Kem. Folyoiral*, 1965, **71**, 304 (*Chem. Abstr.*, 1965, **63**, 12321b).
22. C. Grundmann and A. Kreutzberger, *J. Amer. Chem. Soc.*, 1954, **76**, 632.
23. C. Grundmann and A. Kreutzberger, *J. Amer. Chem. Soc.*, 1954, **76**, 5646.
24. J.E. O'Reilly and P.J. Elving, *J. Amer. Chem. Soc.*, 1972, **94**, 7941.
25. E.Yu. Khmelnitskaya, *Elektrokhimiya*, 1975, **11**, 873.
26. M. Privman and P. Zuman, unpublished.
27. V.A. Korolev, M.A. Mal'tseva, and N.A. Andronova, *Zh. Obshch. Khim.*, 1975, **45**, 243.
28. P. Zuman and R. Patel, *"Techniques in Organic Reaction Kinetics,"* J. Wiley & Sons, New York, 1984, pp. 147-149.
29. A. Albert and J.N. Phillips, *J. Chem. Soc.*, 1956, 1294.
30. V.A. Korolev and M.A. Mal'tseva, *Zh. Obshch. Khim.*, 1976, **66**, 1605.
31. T. Brinck, J.S. Murray, P. Politzer, and R.E. Carter, *J. Org. Chem.*, 1991, **56**, 2934.

Received, 12th October, 1993