San Fernando Valley State College

SYNTHESIS AND FORMOLYSIS OF A TRIAZINYLPROPYL BROSYLATE

A thesis submitted in partial satisfaction of the requirements for the degree of Master of Science in Chemistry

by

David Arthur Davenport

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The thesis of David Arthur Davenport is approved:

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To

My Family And Friends
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ABSTRACT

SYNTHESIS AND FORMOLYSIS OF A TRIAZINYLPROPYL BROSYLATE

by

David Arthur Davenport

Master of Science in Chemistry

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Methyl acetate was condensed with 2,4,6-trimethyl-5-triazine to give the enol, 1-(4,6-dimethyl-5-triazin-2-yl)-prop-1-en-2-ol. The enol was catalytically reduced to the alcohol, 1-(4,6-dimethyl-5-triazin-2-yl)-2-propanol. The p-bromobenzenesulfonate ester of the alcohol was prepared and formolyzed at 25.00° to give a rate constant of \( k = (2.75 \pm 0.21) \times 10^{-4} \text{ sec}^{-1} \). The rate enhancement, relative to the estimated value, is discussed and a possible explanation is presented.
CHAPTER I

INTRODUCTION

_s-Triazine_ compounds are characterized by the presence of an unsaturated six-membered ring containing alternating carbon and nitrogen atoms (1). Because of the symmetry, the ring is designated as _s-_triazine or 1,3,5-triazine. Thus, it is distinguished from the other two isomeric ring structures, _as-_triazine or 1,2,4-triazine and _v-_triazine or 1,2,3-triazine.

Many _s-_triazine derivatives have been synthesized for their commercial use as agricultural biocides, surface active compounds, dye intermediates, polymer intermediates, pharmaceutical intermediates, intermediates for antibacterial agents, fumigants, and insecticides. As a secondary result of these syntheses, considerable knowledge has been gained concerning the chemical behavior of the _s-_triazine ring. However, relatively few studies have been directed
primarily towards gaining insight into the mechanistic behavior of the \textit{s}-triazine ring itself. The present study was undertaken for the purpose of studying the effect of a neighboring triazinyl group on solvolysis. More specifically, this study is concerned with the synthesis and formolysis of the \textit{p}-bromobenzenesulfonate ester of 1-(4,6-dimethyl-\textit{s}-triazin-2-yl)-2-propanol (2).

This compound with the 4,6-dimethyl-\textit{s}-triazin-2-yl group (3) was chosen rather than the corresponding compound with the unsubstituted \textit{s}-triazinyl group because there was some concern as to whether or not the unsubstituted \textit{s}-triazinyl group could withstand some of the reaction conditions that were anticipated. This concern was brought about because of the known ease of hydrolysis of the parent compound,
s-triazine, in acidic, neutral, or basic aqueous solutions.¹

Our interest in the solvolysis of the triazinyl brosylate (2) was an extension of the results which were obtained earlier by Wolfe.² He determined the substituent constants for the 4,6-dimethyl-s-triazin-2-yl group (3) and found it to be electron withdrawing as is indicated by his values in Table I.

Table I

Substituent Constants for the
4,6-Dimethyl-s-triazin-2-yl Group

\[
\begin{align*}
\sigma_P & = +0.39 \\
\sigma_m & = +0.25 \\
\sigma_I & = +0.15 \\
\sigma_{PR} & = +0.24 \\
\sigma_{mR} & = +0.10
\end{align*}
\]

The values for the Hammett sigmas (\(\sigma_P\) and \(\sigma_m\)) were obtained by determining the ionization constants of the corresponding substituted benzoic acids. Then by utilizing Taft's empirical equation,³ the Hammett sigma values were separated into an inductive sigma value (\(\sigma_I\)) and the corresponding resonance sigma values (\(\sigma_{PR}\) and \(\sigma_{mR}\)). A review of substituent constants has been written by Wells.⁴
In view of these results, it was of interest to determine the effect which the triazinyl group (3) would have on the rate of solvolysis. It was anticipated in view of the substituent constants, that the electron withdrawing ability of the 4,6-dimethyl-s-triazin-2-yl group (3) would decrease the first-order rate of formolysis relative to

\[
\text{OBS} \\
\text{CH}_3 - \text{CH} = \text{CH}_3
\]

isopropyl p-bromobenzenesulfonate (4). As the brosylate anion leaves with the pair of bonding electrons, as illustrated in 5, a positive charge, \(\delta^+\), develops on carbon number two. Since the triazinyl group (3) is electron withdrawing, its inductive effect, relative to hydrogen, would cause carbon number two to become even more positive \(\delta_b^+\). This would make it more difficult for the brosylate anion to leave, and hence increase the energy of activation
and decrease the rate of solvolysis.

A rough estimate of the anticipated relative rate of formolysis of the triazinyl brosylate (2) can be obtained. It is assumed in this estimation that only the inductive effect of the substituent is operable and that no resonance effect or anchimeric assistance occurs. Based only upon Taft's polar substituent constants, which are directly proportional to the inductive effect, Streitwieser\(^5\) has calculated that the acetolysis rate of a \(\beta\)-phenyl substituted brosylate, such as 1-phenyl-2-propyl \(p\)-bromobenzenesulfonate (6), should be approximately one-

\[
\text{ObS}
\]
\[\text{CH}_2-\text{CH-CH}_3\]
\[\text{6}\]

eighth as fast as that of the corresponding unsubstituted brosylate, such as 4. This value has also been assumed to apply in formolysis.\(^6\) Other workers have derived a factor of one-tenth.\(^7\) Experimentally, compound 6 is found to undergo acetolysis one-half as fast\(^8\) as the unsubstituted compound (4). Therefore, the rate is four times faster than that calculated, if only the inductive effect were operable. This fourfold enhancement of rate over the calculated value is attributed to anchimeric assistance.
Utilizing the above factor of one-eighth and the Hammett equation,

$$\log \frac{k}{k_0} = \rho \sigma$$

(1)

where $k$ is the rate constant of the substituted case, $k_0$ is the rate constant of the unsubstituted case, $\rho$ is the reaction constant, and $\sigma$ is the substituent constant, the relative formolysis rate of the triazinyl brosylate (2) in which only the inductive effect is operable may be predicted as follows. The predicted formolysis rate constants of the triazinyl brosylate (2) and the corresponding phenyl compound are represented as $k_t$ and $k_p$, respectively. It is assumed that $\rho$ remains constant for the formolysis of the unsubstituted and substituted isopropyl brosylates. The sigma values used are the inductive sigma values for the corresponding substituents.\textsuperscript{2,3}

$$\log \frac{k_t}{k_0} = \rho (0.15)$$

(2)

$$\log \frac{k_p}{k_0} = \rho (0.09)$$

(3)

$$\frac{k_p}{k_o} = \frac{1}{8}$$

If equation (2) is divided by equation (3) the following expression is obtained:
\[
\frac{\log \frac{k_t}{k_0}}{\log \frac{1}{8}} = \frac{\rho}{\rho} (0.15)
\]

\[
\log \frac{k_t}{k_0} = (-0.903) (1.67) = -1.51
\]

\[
\log \frac{k_0}{k_t} = 1.51
\]

\[
\frac{k_0}{k_t} = 32
\]

This result, in a very qualitative way, indicates that the formolysis rate of the triazinyl brosylate (2), if determined only by the inductive effect, would be slower than the rate of the unsubstituted isopropyl brosylate (4) by a factor of approximately 32. Any large enhancement of the rate over this calculated value could be attributable to anchimeric assistance. These results are summarized in Table II.

The initial synthetic scheme (Scheme I) for this study involved starting with the preparation of 2,4,6-trimethyl-s-triazine (9) via the free base (8) of ethyl acetimidate hydrochloride (7). The next step was to be the acylation of one of the methyl groups by a Claisen-type condensation to give the ketone (10) as described by Levine. The plan was then to reduce the ketone function to an alcohol (11) and to make the p-toluenesulfonate or p-bromobenzene-sulfonate ester (2) of the alcohol.
Table II

Some Observed and Predicted Formolysis Rates
25.00°

<table>
<thead>
<tr>
<th>Compound</th>
<th>k (sec⁻¹)</th>
<th>Relative Rate</th>
<th>Rate Enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CH₃CH (OBS) CH₃</td>
<td>(4)</td>
<td>6.11 x 10⁻⁵</td>
<td>1</td>
</tr>
<tr>
<td>2. C₆H₅CH₂CH (OBS) CH₃</td>
<td>(6)</td>
<td>7.65 x 10⁻⁶</td>
<td>1/8</td>
</tr>
<tr>
<td>3. C₆H₅CH₂CH (OBS) CH₃</td>
<td>(6)</td>
<td>3.01 x 10⁻⁵</td>
<td>1/2</td>
</tr>
<tr>
<td>4. CH₂CH (OBS) CH₃</td>
<td>(2)</td>
<td>1.91 x 10⁻⁶</td>
<td>1/32</td>
</tr>
</tbody>
</table>

aConsidering only the inductive effect.
Initial Synthetic Scheme

1. $\text{KHN}_2, \text{NH}_3$
2. $\text{CH}_3\text{COOCH}_3$
3. $\text{H}^+$

Solvolyis

1. $\text{TsCl or BscI}$
2. $\text{Pyridine}$

$\text{NaBH}_4$

1. $\text{H}_2/\text{PtO}_2$
2. (Ethanol)
CHAPTER II

RESULTS AND DISCUSSION

A. Actual Synthetic Scheme

The synthetic routes that actually materialized are given in Scheme II.

B. Preparation of the Triazinyl Alcohols

The product resulting from the acylation of trimethyl-s-triazine (9) was reported as existing in the keto (10) and enol form. This description of the product caused a number of problems in purification and subsequent reactions. The product was eventually found to be the pure enol, i.e. 1-(4,6-dimethyl-s-triazin-2-yl)prop-1-en-2-ol (12). Initially the crude product from the preparation of the enol (12) did indeed show evidence of both a carbonyl group and a carbon-carbon double bond (ir: 1700 and 1640 cm\(^{-1}\) respectively), as well as a wide melting point range.
SCHEME II

Actual Synthetic Scheme

1.) $7 \xrightarrow{aq. \text{K}_2\text{CO}_3} 8 \xrightarrow{\text{trimerize}, \text{H}^+ (\text{cat.})} 9$

1.) $\text{KNH}_2, \text{NH}_3$
2.) $\text{CH}_3\text{COOCH}_3$
3.) $\text{H}^+$

$\xrightarrow{ \text{H}_2/\text{Ra-Ni}, \text{cyclohexane} } \xrightarrow{2.2 \text{ eq. BsCl}, \text{pyridine}} \xrightarrow{ \text{2 eq. Et,BsCl}, \text{pyridine} }$

2.2 eq. BsCl
pyridine

Formolysis

$\xrightarrow{\text{CH}_3\text{OH}, \text{EtO}} 1.) \text{CH}_3\text{OH}, \text{EtOH}$
2.) $\text{HCl}$
3.) $\text{NH}_3, \text{CH}_3\text{OH}$

$\xrightarrow{ \text{15} } \xrightarrow{ \text{HCl}, \text{CH}_3\text{OC}_2\text{H}_5, \text{HCl} } \xrightarrow{ \text{HCl, ethanol} } \xrightarrow{\text{14} }$
At various stages of purification, utilizing several methods, it was found that the infrared intensity of the carbonyl band was decreased as a result of the removal of a by-product, which had a carbonyl band but no \textsubscript{s}-triazine band. Upon completion of purification, a yellow product was obtained and shown to be the enol (12). The product gave no evidence of a carbonyl group, but there was also no evidence of any O-H stretching in the 3600-3500 cm\textsuperscript{-1} region as anticipated for the enol form. This absence is now attributed to strong intramolecular hydrogen bonding.\textsuperscript{11} Additional evidence for the enol form was given by the nmr which gave a one proton signal at \( \delta 14.00 \) for an enolic hydroxyl group, a one proton signal at \( \delta 5.4 \) for a vinylic hydrogen, and no signal in the vicinity of \( \delta 3-4 \) where an active methylene group would absorb. The uv also gave evidence of an extended conjugated system relative to that of the \textsubscript{s}-triazine ring (\textsubscript{s}-triazine ring (9), \( \lambda_{\text{max}} 265 \text{ m}\mu \); enol (12), \( \lambda_{\text{max}} 298 \text{ m}\mu \)). Further support for the product being essentially or exclusively the enol (12) was the sharpness of its melting point (66.8-67.8\textdegree).

Preliminary studies\textsuperscript{12} by X-ray diffraction of compound 12 indicate that the molecule is planar and it appears that the carbon-oxygen bond is a single bond.

The by-product carbonyl compound mentioned above had a melting point, a mixture melting point, and ir, and nmr spectra consistent with 4-acetamido-2,6-dimethylpyrimidine
Levine\(^9\) has proposed that the triazinyl ketone (10) is rearranged via the enol (12) into compound 13 in the presence of water. This information indicated the possible presence of water in the reactions, and consequently many precautions were taken. The greatest improvement in the yield of 12 occurred when the absolute ether, used as a solvent, was first distilled from lithium aluminum hydride.

A difficulty arising from the product being the pure enol (12) occurred in the attempted reduction of the product to the triazinylpropyl alcohol (11). The absence of any keto form, no doubt accounts for the failure of sodium borohydride to reduce the enol (12) to the alcohol (11). Lithium aluminum hydride reduction was not attempted because of its known ability to reduce the triazine ring.\(^{13}\) Hydrogenation with platinum oxide in commercial absolute ethanol was not reproducible, yielding at different times no change, desired product, and ring reduction. A control with just the enol (12) and commercial absolute ethanol gave partial conversion to compound 13. As a result of this evidence a series of controls were run with the enol
(12) in various solvents to determine in which solvent the formation of compound 13 was minimal. Cyclohexane gave the best results. However, due to the difficulties encountered in the platinum catalyzed reduction, this specific method was discontinued and other methods of reduction of the enol (12) were considered.

Concurrently the synthesis of an alternate system for solvolysis was begun, namely, the preparation of 2-(2-hydroxyethyl)-4,6-dimethyl-5-triazine (14). This synthesis involved the cotrimerization of the amidine salt, 3-hydroxypropionamidine hydrochloride (15), with ethyl acetimidate (8) (see Chapter III, Experimental).

After the synthesis of compound 14 was under way, success in the reduction of the enol (12) was realized by the use of hydrogen and Raney nickel in cyclohexane. Consequently, the synthesis of both triazinyl systems (ethyl and
propyl) was continued until success was realized in the preparation of the brosylate of the triazinylpropyl alcohol (2).

C. Preparation of the Sulfonate Esters

In the preparation of the sulfonate esters for solvolysis, the reaction time and relative concentration of reactants were found to be important. The reaction time had to be limited to two hours or there was spectral evidence of structural change in the \( \text{s-triazine} \) ring. Regardless of the time involved there was also evidence of unreacted starting material in the work up when 1.0 or 1.1 equivalents of \( \text{p-toluenesulfonyl chloride} \) were used relative to one equivalent of the alcohol. This problem was resolved by utilizing a 2.2 equivalent ratio of the sulfonyl chloride to the alcohol as suggested by Tipson\(^{14} \) in the preparation of tosyl apocupriene.

D. Formolysis

The formolysis reactions were followed by titrating the \( \text{p-bromobenzenesulfonic acid} \) formed with a solution of sodium acetate in acetic acid. The titrations were followed potentiometrically and the millivolts versus the corresponding milliliters of added sodium acetate solution were plotted. The equivalence points were taken as the inflection points of the curves.

In the formolysis of the triazinyl brosylate (2), a
A preliminary run was made and the results showed that the rate was much faster than anticipated. Consequently, in the next run the aliquots were removed at appropriate times, but the potentiometric titration curves turned out to be relatively linear with no inflection point. According to Marshall\textsuperscript{15} this phenomenon is not uncommon in the potentiometric titrations of formolysis reactions, and he suggested that the titrations be performed in \textit{p}-dioxane-acetic acid (1:1) instead of pure acetic acid. A control titration run on the isopropyl brosylate (4) with \textit{p}-dioxane present gave no change in the titration values. Consequently, the titrations from the formolysis of the triazinyl brosylate (2) were carried out in \textit{p}-dioxane-acetic acid (1:1) and normal curves with readable inflection points were obtained. The \textit{p}-dioxane also served as a quenching agent for the formolysis samples before titration, and the result of a control on its effectiveness is reported in Chapter III, Experimental.

A summary of the conditions and the experimental rates obtained in this study is shown in Table III. A summary of the results determined from the data in Table III is shown in Table IV. (Experimental data is given in Tables V, VI, and VII.)

The final rate constants were obtained by averaging the individual rate constants calculated within each run (see Chapter III, Experimental). The following methods
# Table III

**General Tabulation of Experimental Data: Formolysis**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (moles/l.)</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Average Rate Constant (sec⁻¹)</th>
<th>Experimental Data Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Isopropyl</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Benzobenzene-sulfonate (4)</td>
<td>0.08002</td>
<td>HCOOH</td>
<td>25.00</td>
<td>( (5.73\pm0.06) \times 10^{-5} )</td>
<td>43</td>
</tr>
<tr>
<td><strong>Triazinylpropyl</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Benzobenzene-sulfonate (2)</td>
<td>0.04224</td>
<td>HCOOH</td>
<td>25.00</td>
<td>( (2.94\pm0.21) \times 10^{-4} )</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>0.03812</td>
<td>HCOOH</td>
<td>25.00</td>
<td>( (2.55\pm0.08) \times 10^{-4} )</td>
<td>45</td>
</tr>
</tbody>
</table>
## Table IV
General Tabulation of Formolysis Results

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate Constant (sec⁻¹)</th>
<th>Half-Life</th>
<th>Relative Rate</th>
<th>Predicted Relative Rate (See Table II)</th>
<th>Rate Enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Bromobenzene-sulfonate (4)</td>
<td>(5.73 ± 0.06) x 10⁻⁵ᵃ</td>
<td>3.36 hr</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Triazinylpropyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Bromobenzene-sulfonate (2)</td>
<td>(2.75 ± 0.21) x 10⁻⁴</td>
<td>42 min</td>
<td>4.8</td>
<td>1/32</td>
<td>154</td>
</tr>
</tbody>
</table>

ᵃ Compared to 6.11 x 10⁻⁵ sec⁻¹ obtained by Winstein.¹⁰
were also examined for determining the rate constant for the triazinyl brosylate (2), but judged not to be significantly different or more reliable. Extrapolation to \( t = 0 \) on plots of \( k \) versus time gave approximate values for \( k \) of \( 3.3 \times 10^{-4} \) sec\(^{-1} \) and \( 2.8 \times 10^{-4} \) sec\(^{-1} \), respectively, for the first and second formolysis runs of the triazinyl brosylate (2). The determination of \( k \) from the slope of a visually drawn best-fit straight line through the points of a plot of \( \log a/a-x \) versus time gave an approximate value of \( 2.4 \times 10^{-4} \) sec\(^{-1} \) for both formolysis runs of the triazinyl brosylate (2). A non-weighted least-squares treatment of the above plots did not give representative values because of the influence of those points at large values for time.

It was noticed that in each formolysis run on the triazinyl brosylate (2) the rate constants drifted downward quite noticeably after approximately one half-life (see Tables VI and VII). A possible reason for this drift, in addition to a common ion effect, may be that the \( \text{p-bromo-benzenesulfonic acid (BsOH)} \) generated in the formolysis reaction is a strong enough acid \( (K_a = 10^{-2}) \) to significantly protonate the triazine ring as shown in equation (4). As the reaction proceeds the BsOH concentration
increases, and consequently the concentration of the protonated triazinyl brosylate increases. Because of the added inductive effect caused by the positive charge on the ring, it is reasonable that the rate of ionization during formolysis of the protonated species would be slower than that of the unprotonated species. Marshall proposed a similar explanation to account for the downward drifting rate constant encountered in the acetolysis of the β-anisylethyl tosylates. The above explanation may be evaluated semiquantitatively if the conjugate acid of the triazinylpropyl brosylates is assumed to have an equilibrium constant \( K_a(\text{triazineH}^+) \) equal to that of the conjugate acid of 3,5,6-trimethyl-α-triazine \( (K_a = 1.4 \times 10^{-3}) \). The equilibrium constant for reaction (4) may be expressed as \( K = \frac{K_a(\text{BSOH})}{K_a(\text{triazineH}^+)} \). The value of approximately seven for the equilibrium constant indicates a position of equilibrium considerably to the right. If the downward drift of the rate constant is due to protonation of the brosylate, this could be minimized by carrying out the formolysis in the presence of formate ion so as
to neutralize the BsOH as it is formed.

After the titrations were completed the solvents were distilled off under reduced pressure. The ir spectrum of the residue showed the anticipated bands, including that of the triazine ring. The products were not further identified.

Two possibilities come to mind as conceivable explanations for the rate enhancement of the neighboring triazinyl group (3). The first possibility involves anchimeric assistance by the triazinyl group (3) leading to the formation of a triazinonium ion (16) analogous to the phenonium
ion. However, this would require that some positive charge exist on the nitrogen atoms within the triazine ring as illustrated by the contributing structures $^{16}$ a, b, c. This is not a particularly attractive situation as brought out by the fact that in the sulfonation ($\text{SO}_3$ in liquid $\text{SO}_2$) of 2,6-di-t-butylpyridine, $^{17}$ the major product is the 3-substituted pyridine rather than the 4-substituted pyridine. This reaction has been shown to occur on the free base because the tertiary butyl groups serve to prevent the formation of the pyridinium salt. Thus, the free base shows a preference for substitution on the 3-position which places positive charge on the carbons in the 2-, 4-, and 6-position, and avoids placing any positive charge on the nitrogen which would be the consequence of substitution on the 4-position.

In order to evaluate the feasibility of the triazinonium ion in view of the above, a comparison is made with the analogous phenyl compound, 1-phenyl-2-propyl brosylate (6). Upon formolysis, compound 6 is postulated$^8$ as proceeding via a phenonium ion in which positive charge is placed on carbon atoms. However, its rate is only one-half that of
the unsubstituted compound. Therefore, it does not appear reasonable to postulate a less feasible triazinonium ion with positive charge on the nitrogens in order to explain a rate enhancement of 4.8 over the unsubstituted compound (see Table IV).

The second possibility involves the partial formation of a four-membered ring or the invoking of back-side assist by the unshared pair of electrons of the nitrogen. Although it is known\(^{18}\) that intact four-membered rings do not form as readily as three or five and six-membered rings, it should be pointed out in this case that the realization of a fully-formed four-membered ring is not postulated or necessary. The proposed intermediate (17) is not considered to be capable of leading to rearranged products, but, nevertheless, its formation would offer anchimeric assistance to the ionization and would maintain configuration.
It should be noted that although nitrogen bears a partial positive charge in this intermediate, it arises from sharing its previously unshared pair of electrons (as in an ammonium ion) and not as a result of donating a pair of electrons and destroying its octet as in the triazinonium ion.

Obviously, the elucidation of the mechanism which is responsible for the observed rate enhancement will require further studies. These studies may include acetolysis,
identification of solvolytic products, isotopic labeling experiments, stereochemical studies and synthesis and solvolysis of similar systems.
CHAPTER III

EXPERIMENTAL

A. General

All melting points are uncorrected and were taken in an open capillary tube in a stirred silicone oil bath using Anschuetz thermometers.

All infrared spectra were taken on a Beckman IR-8 Infrared Spectrophotometer unless otherwise noted.

All nmr spectra were taken on a Hitachi R-20 nmr Spectrometer operating at 60 MHz.

Analyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, New York; Galbraith Laboratories, Inc., Knoxville, Tennessee; and Elek Microanalytical Laboratories, Torrance, California.

B. Synthesis

Ethyl Acetimidate Hydrochloride (7). This compound was prepared by the method of Schaefer and Peters. Acetonitrile (492.6 g, 12 mol, dried over and distilled from fresh molecular sieve #4A), and 552.8 g (12 mol) of absolute ethanol (distilled from sodium) were dissolved in 1000 ml of benzene (dried over and distilled from fresh
sodium), contained in a dried 4-l. filter flask fitted with a cork containing a sintered glass gas bubbling tube and a drying tube attached to the side arm. The assembly and its contents were weighed and then placed in a mixture of ice, water, and salt. Hydrogen chloride gas was passed through a drying tube containing phosphorus pentoxide and then bubbled into the cooled reaction mixture until 476 g (13 mol) of hydrogen chloride had been absorbed (160 min). The mixture was kept cold and stirred with a magnetic stirrer during the addition, after which the system and the bath were allowed to come to room temperature with stirring. The product solidified within 16 hr. If the reaction mixture was permitted to stand for approximately five days, the yield was greatly improved. The material was chilled to 0°, broken up with a stirring rod and filtered. The product was pumped with moderate vacuum as dry as possible under a rubber dam on the filter and then dried under moderate vacuum in a desiccator to give 1385 g (93.5%) mp 107.5-110° (lit.¹⁹, yield 90-100%, mp 110-115°).

**Ethyl Acetimidate (8).** This compound was prepared according to the method of Schaefer and Peters.¹⁹ Ethyl acetimidate hydrochloride (7) (617.75 g, 5 mol) was added quickly at 20-25° to a vigorously stirred mixture of 875 ml of methylene chloride and 718.65 g (5.2 mol) of potassium carbonate dissolved in 2500 ml of water. The organic phase was separated after mixing for 7-10 min, and then the
aqueous phase was re-extracted by mixing with 500 ml of fresh methylene chloride for 30 min, followed by two additional extractions with 100-ml portions of fresh methylene chloride. The extracts were combined and dried \((\text{K}_2\text{CO}_3)\) overnight in a refrigerator. The extract was concentrated by rapid distillation of the solvent through an efficient Vigreux column until the boiling point could no longer be held below 60°. The crude residue (84.8% yield by weight) contained 85-90% ethyl acetimidate, as shown by titration of an aliquot to the methyl orange end point with standard acid, to give an overall yield of 76% (lit.\(^{19}\), 80-85%). This material was suitable for conversion to 2,4,6-trimethyl-s-triazine.

2,4,6-Trimethyl-s-triazine \((\mathbf{9})\). This compound was prepared according to the method of Schaefer and Peters.\(^{19}\) To an 80-85% ethyl acetimidate concentrate \((2.898 \text{ mol})\) prepared as described above was added gradually \((20-30 \text{ min})\) eight mole per cent of glacial acetic acid \((13.3 \text{ ml, } 0.232 \text{ mol})\), based on the imidate content. The reaction mixture was held at 25-30° during the addition and for the following hr, after which the mixture was stirred at room temperature for 16 hr. It was then stripped of most of the ethanol formed, and the resulting residue was diluted with 2-3 volumes \((500 \text{ ml})\) of methylene chloride. The solution was filtered from the acetamidine acetate which had crystallized, and the residual acetic acid was neutralized by
mixing with solid potassium carbonate and a minimum volume of water. The methylene chloride solution was separated from the aqueous phase, dried (CaCl₂), and the solvent was stripped off to give a residue which upon cooling gave a crystalline product which was filtered and dried. The mother liquor was distilled at atmospheric pressure and the product was collected at 150-155°. The combined products gave a yield of 101.45 g (85.5%) (lit.¹⁹, 85-90%), mp 59-61°. The center cut of a portion of sublimed product gave a mp of 59.8-60.8° (lit.²⁰, mp 59-60°, hexane). This compound sublimes quite rapidly at atmospheric pressure.

The best overall yield in this three step synthesis of 2,4,6-trimethyl-s-triazine was 41.3%.

1-(4,6-Dimethyl-s-triazin-2-yl)prop-1-en-2-ol (12). This compound is the enol form of 2,4-dimethyl-6-acetonyl-s-triazine (10). The preparation of the keto form is reportedly given by Osborn, Wieder, and Levine.⁹ Their procedure was followed but the product realized was the enol. A 1-l. three-necked round-bottom flask was equipped with a dropping funnel, a Dry Ice-acetone condenser, and a Hershberg stirrer. All glassware had been previously washed thoroughly, rinsed with distilled water and dried in an oven, and then, after complete assembly the entire apparatus was flamed. The anhydrous ammonia (Matheson Co., Inc.) was passed through a drying tube (CaSO₄) and liquefied on the Dry Ice-acetone condenser until the necessary
amount had been collected. A few rusty tacks were added to the liquid ammonia. Potassium metal, freshly cut under mineral oil, rinsed in 60-90° petroleum ether, and blotted dry, was added in small portions. The potassium amide was used immediately after preparation. The ethyl ether (absolute ether, analyzed reagent, MCB, EX 190) was distilled from lithium aluminum hydride, and the methyl acetate (MCB, Chromatoquality reagent, 99 + mol%, MX625) was dried (molecular sieve and CaCl₂) and distilled (56.0-57.0°) before using.

To potassium amide (0.1 mol) in 150 ml of anhydrous liquid ammonia was added slowly (15 min) a solution of 12.3 g (0.1 mol) of 2,4,6-trimethyl-₃-triazine (9) in 30 ml of anhydrous ether. During the addition, the color of the solution changed from clear to green to yellow to red-brown, color changes occurring at approximately one-tenth, one-half, and complete addition of the ethereal solution of 2,4,6-trimethyl-₃-triazine (9). The resulting solution was stirred for one hr. Methyl acetate (3.7 g, 0.05 mol), dissolved in 10 ml of anhydrous ether, was added slowly (15 min), and the reaction mixture was stirred for an additional hr. Anhydrous ether, 150 ml, was added slowly to replace the ammonia and the solution was allowed to stir overnight and to come to room temperature. The Dry Ice-acetone condenser was replaced by a Vigreux column, a heating mantle was applied and ether was distilled until no
Evidence of ammonia was detected with litmus in the vapors. Additional anhydrous ether was added to the flask as the distillation progressed. The reaction mixture was then poured into a mixture of crushed ice (made from distilled water) and 11.5 ml of concentrated hydrochloric acid. Any excess acid was neutralized by the addition of solid sodium bicarbonate. After separating the ether phase, the aqueous phase was extracted with two 100-ml portions and ten 50-ml portions of chloroform. The organic phases were dried (MgSO₄) and the magnesium sulfate was filtered off using a sintered glass funnel and washed well with chloroform. The solvents were distilled through a Vigreux column on a steam bath, after which the organic phases were combined and the last traces of solvent were distilled off at atmospheric pressure through a micro Vigreux column. Distillation through a Vigreux column at reduced pressure gave, in addition to 6.5 g (53%) of recovered 2,4,6-trimethyl-s-triazine (9), bp 65-70°/30 mm, 3.85 g (46.6%) of the yellow compound 1-((4,6-dimethyl-s-triazin-2-yl)prop-1-en-2-ol, bp 94-100°/6 mm: mp 66.8-67.8° after multiple sublimations. The compound sublimes moderately at atmospheric pressure. Bulk purification of the distillate was done by column chromatography using neutral alumina (activity V) and distilled pentane as the eluent. Spectra data: IR (CHCl₃), 3005, 1640, 1540, 1430, 1320, 1040 weak, 910 cm⁻¹; NMR (CDCl₃) δ 2.08 (s, 3 H, =C-CH₃), 2.50 (s, 6 H, ring CH₃), 5.39
Anal. Calcd for C₈H₁₁N₃O (165.20): C, 58.17; H, 6.71; N, 25.44. Found: C, 58.00; H, 6.73; N, 25.74.

(Lit.⁹ for 2,4-dimethyl-6-acetonyl-s-triazine (10): yield 54.1%, bp 94-100°/5 mm, mp 65-66° after recrystallization from 35-60° petroleum ether, and analysis to give C, 58.38 and H, 6.52.)

After sublimation of the above enol (12) had been completed, continued sublimation of the residue gave a white solid, mp 180-183.5°, which was identified as 4-acetamido-2,6-dimethylpyrimidine (13) by mmr 183-185°, with an authentic sample, mp 185-187°, (lit.⁹ mp 186-187°), and by spectral data: ir (CHCl₃), 3440, 3000, 1700, 1600, 1560-1500, 1430, 1390 cm⁻¹; nmr (CDCl₃) δ 2.20 (s, 3 H, COCH₃), 2.45 (s, 3 H, ring CH₃), 2.55 (s, 3-4 H, ring CH₃), 7.80 (s, 1-H, aromatic H), 8.53 (broad s, 1-H, -NH-).

Solvent Controls for Hydrogenation. A sample of the enol (12) (0.05 g) was dissolved in 50 ml of each of the following solvents: ethanol, cyclohexane, ethyl acetate, water, glacial acetic acid, glyme, and tetrahydrofuran. After five days at room temperature each solvent was evaporated and the purity of each residue was determined by mp or appearance (cyclohexane residue mp 63.5-66°).

1-(4,6-Dimethyl-s-triazin-2-yl)-2-propanol (11).
Freshly prepared W-2 Raney nickel (approximately 0.75 g
stored under absolute ethanol) was transferred into a Parr hydrogenation bottle containing 5 ml of cyclohexane (MCB, CX2290). The Raney nickel was swirled well, allowed to settle and the cyclohexane was removed almost completely by pipette. The wash procedure was repeated three times after which 60 ml of cyclohexane was added. 1-(4,6-dimethyl-s-triazin-2-yl)prop-1-en-2-ol (12) (0.75 g, 0.0045 mol) was added directly to the hydrogenation bottle and dissolved. The hydrogenation bottle was placed on a Parr hydrogenator, flushed three times without pulling a vacuum and charged to approximately 53 psi. The progress of the reduction was followed by uv and appeared to be complete within 28 hr: compound 9, \( \lambda_{\text{max}} \) at 265 \( \mu \)m, compound 12, \( \lambda_{\text{max}} \) at 296 \( \mu \)m, and compound 11, \( \lambda_{\text{max}} \) at 265 \( \mu \)m. As the catalyst aged, more Raney nickel and longer times were required for complete reduction. The mixture was filtered through a Buchner funnel with a slight vacuum and the Raney nickel catalyst began to ignite even as filtration was completed. The cyclohexane was stripped off under vacuum on a rotary evaporator to yield 0.605 g (80.8%) of a liquid that crystallized on standing. Sublimation of the crude product gave pure material which sublimed moderately at atmospheric pressure and was quite hygroscopic: mp 34.0-35.5°; ir (neat) 3420, 3000, 2960, 1540, 1430, 1120, 1050, 950 cm\(^{-1}\); nmr (CDCl\(_3\)) \( \delta \) 1.30 (d, 3 H, CCH\(_3\)), 2.60 (s, 6 H, ring CH\(_3\)), 2.97 (d, 2 H, -CH\(_2\)-), 4.47 (m, 2 H, C-HCOH-C).

1-(4,6-Dimethyl-s-triazin-2-yl)-2-propyl p-Bromo-benzenesulfonate (2). This compound was prepared according to the method of Tipson.¹⁴ Crude 1-(4,6-dimethyl-s-triazin-2-yl)-2-propanol (11) (1.8240 g, 0.01091 mol) was dissolved in 18 ml of pyridine (MCB, PX 2015, for Karl Fischer Reagent) to give a ratio of 100 mg alcohol to one ml of pyridine. The solution was cooled to approximately -5° in an ice salt bath before and during the addition in one portion of 6.1504 g (0.02405 mol) of purified p-bromobenzenesulfonyl chloride (MCB, BX1025), mp 75-76°. The p-bromobenzenesulfonyl chloride was purified by dissolving it in benzene, decanting the solution from the acid impurity, and removing the solvent. For each equivalent of alcohol, 2.2 equivalents of p-bromobenzenesulfonyl chloride was used as in Tipson's¹⁴ section on tosyl apocupreine. After the p-bromobenzenesulfonyl chloride had dissolved, the pyridine solution was kept at 0° for two hr to give a yellow-gold solution. Water (1.8 ml, 10% of the volume of pyridine) was added in portions (0.18 + 0.18 + 0.18 + 0.36 + 0.90 ml) at intervals of 5 min, with swirling at 0°, after which the solution was diluted with 18 ml of water. The aqueous pyridine solution was then extracted with three 18-ml portions of chloroform, and the combined chloroform extracts were washed three times with 18 ml ice-cold 6N
sulfuric acid, once with 30 ml cold water, and once with 30 ml cold saturated sodium bicarbonate solution (ice was kept in the separatory funnel at all times). The chloroform solution was dried (Na$_2$SO$_4$) for one-half hr and filtered through a sintered glass funnel. The solvent was then removed under reduced pressure to give 3.0136 g (71.5%) of crude product. The crude product was dissolved in pentane, and the solution was treated with norite-A, filtered, and cooled to -80° to yield a white precipitate. The supernatant liquid was decanted and the white solid was recrystallized again from pentane at -80°. The last traces of solvent were removed at high vacuum for 30-50 min to yield a white powder (51.5% of crude), mp 64-64.5°. This compound was used as soon as possible after recrystallization as it decomposed within hours at room temperature and within a month at -25°. Spectra data: ir (neat) 3005, shoulder 1574, 1540, 1435, 1390, 1370, 1190, 1180, 1100, 1070, 1040, 1020, 915, 890, 760, 610 cm$^{-1}$.

Anal. Calcd for C$_{14}$H$_{16}$N$_3$O$_3$SBr (386.27): C, 43.53; H, 4.18; N, 10.88; Br, 20.69. Found: C, 43.47; H, 4.50; N, 10.66; Br, 20.09.

Isopropyl p-Bromobenzenesulfonate$^{21,22}$ (4). p-Bromobenzenesulfonyl chloride (12.75 g, 0.05 mol) was added in one portion to a solution of 3 g (0.05 mol) of isopropyl alcohol in 50 ml of anhydrous pyridine at 0°. The reaction mixture was shaken and permitted to stand at 1° for several
days after which the solution was pinkish-purple and contained a considerable number of large, long needle crystals. The solution was poured with vigorous stirring into 100 ml of ice-cold 6N hydrochloric acid to yield an oil. The oil was extracted with the aid of approximately 40 ml of carbon tetrachloride, the solution was dried (K₂CO₃), and the solvent was evaporated at room temperature to yield a viscous residue which was induced to crystallize. The solid was purified by reprecipitation from petroleum ether (60-90°) at -80° and dried at 0.1 mm pressure for 2 hr at room temperature: mp 32.5-33.5° (lit. 32.3-34.1°).

3-Hydroxypropionamidine Hydrochloride (15).

Hydrogen chloride (76.7 g, 2.1 mol passed over phosphorus pentoxide) was bubbled into a stirred mixture (0°) of 142 g (2.0 mol) of redistilled 3-hydroxypropanenitrile (MCB, HX525) in 64 g (2.0 mol) of absolute methanol (distilled from sodium) and 250 ml of ether (distilled from lithium aluminum hydride). The absorption was complete in 90 min. The stirrer was raised so that it agitated only the upper ether layer, and the mixture was stirred at 0° for three days during which the lower layer became a thick slurry. The upper ether layer was decanted, and after the slurry was washed with dry ether, it was dissolved in 500 ml of absolute methanol. This solution was added in a continuous stream from a dropping funnel into a solution of 51 g (3.0 mol) of ammonia in 500 ml of methanol at 0°. The initial
cloudy solution cleared up within 10 min and the clear solution was stirred for 1 hr. The solution was subjected to vacuum distillation with the receiver in a Dry Ice-acetone bath. Distillate started collecting at a pressure of about 95 mm and continued as the pressure was lowered to 20 mm. After the distillation had stopped, the liquid in the pot solidified upon cooling to yield 247.5 g (99.4%) (lit.23 200-225 g, 80-90%). Then at least fourteen 100-ml portions of reagent grade isopropyl alcohol were added to dissolve the solid to give 1750 ml of isopropyl alcohol solution which was gravity filtered through a fluted filter paper to remove ammonium chloride. The product was precipitated by the addition of 5250 ml of absolute ether, vacuum filtered through a sintered-glass funnel, dried under a rubber dam and then dried over phosphorus pentoxide in a vacuum desiccator to yield a hygroscopic white solid 179.3 g (72.1%), mp 85-86° (lit.23 mp 84-85.5°).

2-(2-Hydroxyethyl)-4,6-dimethyl-s-triazine24 (14). The ethyl acetimidate was obtained from the ethyl acetimidate concentrate (8) by distillation, bp 88-90°; nD 1.4020 (lit.19 bp 91°, nD 1.4052).

A mixture of 87 g (1.0 mol) of ethyl acetimidate, 50 g (0.40 mol) of 3-hydroxypropionamidine hydrochloride and 15 g of ethanol was heated to 50° in a water bath and mixed until dissolved. The clear yellow solution was permitted to stand for 40 hr at room temperature during which time a
crystalline precipitate formed. The supernatant liquid containing the product was decanted from the crystalline acetamidine hydrochloride and diluted with 350 ml of ether to precipitate additional amidine salt which came out slowly in the form of a slurry. The ether solution was decanted and evaporated on a rotary evaporator to yield 33 g (53.7%) of residue. Distillation of the crude product from the residue was unsatisfactory. Consequently, the product was purified by column chromatography using neutral activated alumina (grade V) and a solvent system progressing from pentane to ether. Recovery of the desired product from the column was 62.4% of the crude product. The analytical sample was distilled at 100° (0.6 mm) from the chromatographed product (lit. bp 89° (1.5 mm)).

Spectra data: ir (CHCl₃) 3450, 3005, 1540, 1420, 1050, 955, 890 cm⁻¹; nmr (CDCl₃) δ 2.62 (s, 6 H, ring CH₃), 3.14 (t, 2 H, -CH₂-), 4.20 (m, 3 H, -CH₂OH).


C. Kinetics

Solvents. The acetic acid solvent was glacial acetic acid (MCB, AX73, 99.8%) that was refluxed for 10 hr with one per cent acetic anhydride.

Formic acid (MCB, 97-100%) was purified in a 1-1. batch. The low boiling components were distilled through
a Vigreux column until the head temperature reached 98.5°. After cooling, boric anhydride (4 g per gram of water, calculated on the basis of 3% water in the formic acid) was added (the boric anhydride had been dried at 200° for two and one-half hr). After standing for three days at room temperature, the formic acid was decanted and distilled from fresh boric anhydride; bp 28-29° (50 mm) (lit.¹⁰ bp 30-31° (50 mm)).

The p-dioxane (MCB, DX2090) was scintillation quality and was not purified further.

Method of Rate Measurements. A weighed amount of p-bromobenzenesulfonate ester was dissolved in and made up to a volume of 50 ml with formic acid at 25.00°. The volumetric flask was vigorously shaken and returned to the constant temperature water bath. A Sargent Thermonitor automatic thermostat maintained the temperature of the water bath at 25.00±0.02°. In the control run on isopropyl brosylate (⁴), the samples were withdrawn with a 5-ml calibrated automatic pipette, quenched by delivery into a beaker containing 50 ml of anhydrous acetic acid and titrated potentiometrically as described below. In the runs with the triazinyl brosylate (²), the samples were withdrawn in the same manner and quenched by delivery into a beaker containing 50 ml of p-dioxane.¹⁵ The time of the beginning of the delivery into the acetic acid or p-dioxane was used in the rate calculations, and the time called zero
for the quenching of the first samples. When a sample from the formolysis of the triazinyl brosylate (2) in p-dioxane was ready to be titrated, 50 ml of anhydrous acetic acid was added, and the titration was carried out immediately. It was necessary to wear cotton clothes to minimize static charge and its effect upon the titration apparatus.

To determine the quenching properties of p-dioxane on the formolysis of the triazinyl brosylate, a 20-ml solution of ca. 0.038 M triazinyl brosylate (2) in formic acid was prepared. After 14 min this solution was mixed with 200 ml of p-dioxane and 55 ml of the resulting solution was withdrawn, added to 50 ml of acetic acid and titrated immediately. After 4 hr, 55 ml was again withdrawn and the procedure was repeated. It was found that formolysis was continuing at a rate corresponding to ca. 0.05 ml of base per hr in p-dioxane. The results in Tables VI and VII are adjusted appropriately for the length of time in p-dioxane before titration.

**Potentiometric Titration.** An IL Deltamatic Model 245 pH meter with standard glass and calomel electrodes was employed. The glass electrode was attached directly to the pH meter, and the calomel electrode was attached to the negative side of a dry cell (1.5 volt) and to one side of a 50,000 ohm variable resistor, R. The middle pole of R was connected to the pH meter (normal connection of the calomel electrode), and the side pole of R was connected to
the positive side of the dry cell. The buret tip was coated with Desicote (Beckman 18772), and the beaker was set in a copper cup which was grounded. The electrodes were immersed in the magnetically stirred solution to be titrated, and the mv reading was adjusted with R and the standardization knob on the pH meter, to an arbitrary setting of 700 mv on the 800 mv scale. The solution was titrated with approximately 0.05 N sodium acetate in acetic acid and the mv readings were plotted against the volume of added base. From the inflection point of the curve, the concentration of acid generated in the reaction was calculated. The sodium acetate solution (0.05006 N) was made up by weight by dissolving fused anhydrous sodium acetate in glacial acetic acid.

Method of Calculation. First-order rate constants for solvolysis rates of the brosylates were calculated with the following equation:

\[ k = \frac{2.303}{t} \log \left( \frac{a_x}{a-x} \right) \]  

Where  
\( a = \) time zero to time infinity change of concentration of brosylate.  
\( x = \) time zero to time \( t \) change of concentration of brosylate.  
\( a-x = \) amount of reactable brosylate left after time \( t \).  
\( t = \) elapsed time in seconds.  
\( k = \) rate constant (sec\(^{-1}\)).
It is not necessary to carry out this calculation using actual concentrations. Hammett\textsuperscript{25} points out the fact that any quantity which is proportional to the concentration may be used even when the proportionality constant is unknown. The corresponding volumes of 0.05N sodium acetate in acetic acid used in the titrations were used in the present calculations.

**Reporting of the Rate Measurements.** The average mean deviation for first-order rate constants is listed with each individual run.

There is evidence of a drifting rate constant and this is discussed in the text of the thesis. In the case of drifting rate constants, the average mean deviation turns out to be somewhat larger than in other runs.

Duplicate runs were made on the triazinyl brosylate at 25.00\(^\circ\) and the average of these two independent runs was taken as the value of the rate constant at 25.00\(^\circ\).

**Kinetic Results.** A general tabulation of the rate data is summarized in Table III. For each determination, the temperature, initial concentration of the reactants, the solvent, the per cent titration at time infinity, as well as the data used in calculating the rate constants are recorded.
Table V
Rate of Formolysis of Isopropyl Brosylate

<table>
<thead>
<tr>
<th>Initial concn of brosylate</th>
<th>0.08002 moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>HCOOH</td>
</tr>
<tr>
<td>Temperature</td>
<td>25.00°</td>
</tr>
<tr>
<td>Per cent reacted at time infinity</td>
<td>100.5%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
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<tbody>
<tr>
<td>Time (sec)</td>
<td>-</td>
<td>5910</td>
<td>14666</td>
<td>31150</td>
<td>42265</td>
<td>129,200</td>
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</tr>
<tr>
<td>Vol of NaOAc 0.05006N</td>
<td>1.16</td>
<td>3.12</td>
<td>5.10</td>
<td>6.89</td>
<td>7.40</td>
<td>7.90</td>
<td>8.03</td>
</tr>
<tr>
<td>a-x</td>
<td>6.87*</td>
<td>4.91</td>
<td>2.93</td>
<td>1.14</td>
<td>0.63</td>
<td>0.13</td>
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</tr>
<tr>
<td>a/a-x</td>
<td>-</td>
<td>1.3990</td>
<td>2.3447</td>
<td>6.0263</td>
<td>10.905</td>
<td>52.846</td>
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<tr>
<td>log a/a-x</td>
<td>-</td>
<td>0.14582</td>
<td>0.37009</td>
<td>0.78005</td>
<td>1.03763</td>
<td>1.72301</td>
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</tr>
<tr>
<td>k (sec^{-1}) x 10^5</td>
<td>-</td>
<td>5.68</td>
<td>5.81</td>
<td>5.77</td>
<td>5.65</td>
<td>3.07</td>
<td></td>
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<tr>
<td>Average k</td>
<td>(5.73±0.06) x 10^{-5} sec^{-1} (omitting point 6)</td>
<td></td>
<td></td>
<td></td>
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</tr>
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</table>

* Taken as value for a.
Table VI

Rate of Formolysis of Triazinylpropyl Brosylate

<table>
<thead>
<tr>
<th>Initial concn of brosylate</th>
<th>0.04224 moles/liter</th>
</tr>
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<tbody>
<tr>
<td>Solvent</td>
<td>HCOOH</td>
</tr>
<tr>
<td>Temperature</td>
<td>25.00°</td>
</tr>
<tr>
<td>Per cent reacted at time infinity</td>
<td>93.6% 44 hr = t_∞</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aliquot</th>
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<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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</thead>
<tbody>
<tr>
<td>Time (sec)</td>
<td>-</td>
<td>129</td>
<td>269</td>
<td>360</td>
<td>601</td>
<td>1801</td>
<td>360</td>
<td>11580</td>
<td></td>
</tr>
<tr>
<td>Vol of NaOAc 0.05006N</td>
<td>0.18</td>
<td>0.34</td>
<td>0.48</td>
<td>0.58</td>
<td>0.81</td>
<td>1.56</td>
<td>2.17</td>
<td>3.22</td>
<td>3.95</td>
</tr>
<tr>
<td>a-x</td>
<td>3.77*</td>
<td>3.61</td>
<td>3.47</td>
<td>3.37</td>
<td>3.14</td>
<td>2.39</td>
<td>1.78</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>a/a-x</td>
<td>-</td>
<td>1.0443</td>
<td>1.0862</td>
<td>1.1187</td>
<td>1.2006</td>
<td>1.5774</td>
<td>2.1180</td>
<td>5.1644</td>
<td></td>
</tr>
<tr>
<td>log a/a-x</td>
<td>-</td>
<td>0.01883</td>
<td>0.03603</td>
<td>0.04871</td>
<td>0.07940</td>
<td>0.19794</td>
<td>0.32593</td>
<td>0.71302</td>
<td></td>
</tr>
<tr>
<td>k (sec⁻¹)</td>
<td>x 10⁴</td>
<td>-</td>
<td>3.36</td>
<td>3.08</td>
<td>3.12</td>
<td>3.04</td>
<td>2.53</td>
<td>2.08</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Average k (2.94±0.21) x 10⁻⁴ sec⁻¹ (omitting points 2, 7 and 8)

* Taken as value for a.
**Table VII**

Rate of Formolysis of Triazinylpropyl Brosylate

<table>
<thead>
<tr>
<th>Initial concn of brosylate</th>
<th>0.03812 moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>HCOOH</td>
</tr>
<tr>
<td>Temperature</td>
<td>25.00°</td>
</tr>
<tr>
<td>Per cent reacted at time infinity</td>
<td>93.2% 49 hr = ( t_\infty )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (sec)</td>
<td>-</td>
<td>196</td>
<td>360</td>
<td>541</td>
<td>846</td>
<td>1200</td>
<td>1800</td>
<td>5400</td>
<td></td>
</tr>
<tr>
<td>Vol of NaOAc 0.05006N</td>
<td>0.26</td>
<td>0.42</td>
<td>0.56</td>
<td>0.70</td>
<td>0.90</td>
<td>1.11</td>
<td>1.40</td>
<td>2.35</td>
<td>3.55</td>
</tr>
<tr>
<td>( a-x )</td>
<td>3.29*</td>
<td>3.13</td>
<td>2.99</td>
<td>2.85</td>
<td>2.65</td>
<td>2.44</td>
<td>2.15</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>( a/a-x )</td>
<td>-</td>
<td>1.0511</td>
<td>1.1003</td>
<td>1.1544</td>
<td>1.2415</td>
<td>1.3484</td>
<td>1.5302</td>
<td>2.7417</td>
<td></td>
</tr>
<tr>
<td>( \log a/a-x )</td>
<td>-</td>
<td>0.02164</td>
<td>0.04192</td>
<td>0.06236</td>
<td>0.09395</td>
<td>0.12982</td>
<td>0.18475</td>
<td>0.43802</td>
<td></td>
</tr>
<tr>
<td>( k ) (sec(^{-1})) ( \times 10^4 )</td>
<td>-</td>
<td>2.54</td>
<td>2.68</td>
<td>2.65</td>
<td>2.56</td>
<td>2.49</td>
<td>2.36</td>
<td>1.87</td>
<td></td>
</tr>
</tbody>
</table>

Average \( k \) \((2.55 \pm 0.08) \times 10^{-4} \) sec\(^{-1}\) (omitting point 8)

* Taken as value for \( a \).
BIBLIOGRAPHY


