method, may be compared with that of $7.78 \times 10^{-6}$ sec$^{-1}$ at 24.85°, determined by conductivity.

By suitable extraction techniques, this method may be used also for reactions in solvents that absorb in this region. Thus, reactions of methyl tosylate in benzene can be followed by extracting aliquots of the reaction mixture with water, back-extracting with cyclohexane, and measuring the absorbance of the water layer. In a number of runs in water, methyl tosylate was determined in cyclohexane after extraction. Similarly, extraction techniques may also be devised for following the reactions of an ester whose absorption is the same as that of the anion produced.

**Experimental**

The procedure used for the reactions in water is described below using the hydrolysis of methyl tosylate as a typical example.

**Water** was laboratory distilled water redistilled from sodium hydroxide-potassium permanganate in an all-Pyrex apparatus. It was degassed by bubbling carbon dioxide-free nitrogen through it for at least 20 min.

Methyl tosylate, Eastman White Label grade, was recrystallized from reagent grade cyclohexane-ether and dried in a desiccator over phosphorus pentoxide at 25°. The ester was allowed to melt, cooled, and a seed crystal was introduced. When approximately 75% of the material had crystallized from reagent grade cyclohexane-ether and dried in a desiccator (calcium sulfate), it for at least 20 min. The methyl tosylate, m.p. 28.4–29.4° (uncorr.), was stored in a desiccator over Drierite (calcium sulfate).

**Kinetics.—**Temperature control was ± 0.02°. The temperature was determined using a thermometer calibrated by the National Bureau of Standards.

A 50-ml volumetric flask was filled to the mark with water under an atmosphere of carbon dioxide-free nitrogen. Approximately 10 ml of methyl tosylate was added and the resulting mixture was shaken vigorously to give the reaction solution, which was placed in a constant-temperature bath at 25°. After 10 min. (zero point), and at suitable times thereafter, a sample of reaction solution was transferred to a glass-stoppered 1-cm. silica cell and its absorbance was determined at 261 mp at a slit width of 0.4 mm, using a Beckman DU spectrophotometer. A Beer's law plot (absorbance vs. fraction sodium tosylate) was linear for the change from methyl tosylate to tosylate anion. The concentration of methyl tosylate present initially was calculated from the change of absorbance of methyl tosylate at 261 mp.

First-order rate constants were obtained from a plot of per cent unchanged methyl tosylate vs. time on semilogarithmic paper by dividing 0.693 by the half-life. Data for a typical run are shown in Table I.

**Table I**

<table>
<thead>
<tr>
<th>Time, hr.</th>
<th>Absorbance</th>
<th>% unchanged</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.791</td>
<td>100.0</td>
</tr>
<tr>
<td>5</td>
<td>0.746</td>
<td>87.9</td>
</tr>
<tr>
<td>9</td>
<td>0.709</td>
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<tr>
<td>24</td>
<td>0.611</td>
<td>51.5</td>
</tr>
<tr>
<td>32</td>
<td>0.570</td>
<td>40.4</td>
</tr>
<tr>
<td>44</td>
<td>0.526</td>
<td>28.6</td>
</tr>
<tr>
<td>55</td>
<td>0.498</td>
<td>21.0</td>
</tr>
<tr>
<td>67</td>
<td>0.471</td>
<td>13.7</td>
</tr>
<tr>
<td>290</td>
<td>0.420</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$k_1 = 7.91 \times 10^{-6}$ sec$^{-1}$

In a previous study, the reaction of α-pinene oxide (I) with glacial acetic acid was reported to give campholenaldehyde (II) and a high boiling fraction which was apparently a crude hydroxycacetate. Arbuzov and Mikhailov have reported the formation of a glycol monocacetate on treatment of α-pinene with peracetic acid in chloroform solution, and that a similar product was obtained on treatment of α-pinene oxide with acetic acid.

We have reinvestigated the reaction of dl-α-pinene oxide with a solution of sodium acetate in glacial acetic acid and found it to afford 39% campholenaldehyde, 19% dl-trans-carveol (III), and 23% dl-trans-8-acetoxy-6-hydroxy-1-p-menthene (IV). Identity of the latter product was established by saponification to dl-trans-sobrerol, and by pyrolysis to yield dl-trans-carveol (III) as the only product.

Inasmuch as the conversion of α-pinene oxide in this and previously reported work to sobrerol or its derivatives has invariably afforded the trans isomers, the stereochemistry of the epoxide must be as shown in I, the influence of steric hindrance playing a role similar to that observed for pinol.

In view of the present results, the theoretical arguments of Brewster, and the hydrogenation of the higher rotating carvotanacetol to the carvomenthol having the hydroxyl trans to the isopropyl group, we must conclude that the generally accepted con-

\[ \text{H}_2\text{C}_\text{CH}_3 \]

\[ \text{HOAc} \]

\[ \text{OAc}^- \]

\[ \text{CH} \]

\[ \text{OH} \]

\[ \text{H} \]

\[ \text{O} \]

\[ \text{CH}_3 \]

\[ \text{O} \]

\[ \text{C} \]

\[ \text{CH}_3 \]

\[ \text{HOAc} \]

\[ \text{OAc}^- \]

\[ \text{CH} \]

\[ \text{OH} \]

\[ \text{H} \]

\[ \text{O} \]

\[ \text{CH}_3 \]

\[ \text{O} \]

\[ \text{C} \]

\[ \text{CH}_3 \]

\[ \text{O} \]

\[ \text{C} \]

\[ \text{CH}_3 \]

\[ \text{O} \]

\[ \text{C} \]

\[ \text{CH}_3 \]

\[ \text{O} \]

\[ \text{C} \]

\[ \text{CH}_3 \]

\[ \text{O} \]

\[ \text{C} \]

\[ \text{CH}_3 \]

\[ \text{O} \]

\[ \text{C} \]
An Improved Synthesis of Peroxybenzoic Acid

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Peroxybenzoic acid is commonly prepared by a two-step process. In the first step, benzoyl chloride reacts with aqueous sodium peroxide. Because benzoyl chloro-}

ride is immiscible with the solution, the reaction with the hydroperoxide ion (eq 1) takes place at the surface of the droplets. The peroxybenzoate anion is less reactive toward benzoyl chloride than is HOCO⁻, but reacts preferentially (eq 2) because it is in contact. Several experimental procedures have been given.¹⁻²

In the second step, benzoyl peroxide is cleaved by sodium methoxide (eq 3). The procedure described by Braun has been modified by later workers.³⁻⁶

Kergomard and Bigou and Vilka have reported a method which avoids the formation of benzoyl peroxide. Sodium peroxide, or equivalent amounts of hydrogen peroxide and sodium hydroxide, is dissolved in a mixed solvent system in which benzoyl chloride is also soluble. In such a system, the peroxybenzoate ion and the hydroperoxide ion can compete as nucleophiles for benzoyl chloride. Very little benzoyl peroxide is formed. Peroxybenzoic acid can be recovered from the reaction mixture as soon as the addition of benzoyl chloride is complete.

This method is quicker, gives better yields, and is much safer in that neither benzoyl peroxide nor sodium metal is involved. It has the disadvantage of requiring a reaction temperature of -5° or lower.

We have had occasion to repeat many times this last method. We consistently obtain better yields using sodium peroxide rather than hydrogen peroxide and sodium hydroxide. Purification of the sodium peroxide by recrystallization as Na₂O₄·8H₂O gives further improvements in yield. This indicates that cata
dyl decomposition is occurring.

In commercial bleaching operations, the catalytic effect of traces of metal ions is inhibited by adding a small amount of magnesium sulfate. We have found that the addition of a little magnesium sulfate to the reaction mixture allows the reaction to be run at room

Notes

²⁰

⁹ M. Vilka, ibid., 1501 (1959); French Patent 1,177,666 (1958).