The rate law for the above mechanism comes out to be

\[
\frac{-d[Ce^{4+}]}{dt} = \frac{AK[Ce^{4+}][Ru^{3+}][isopropanol]}{1 + K[Ru^{3+}] + K[isopropanol]}
\]

The above rate equation explains the first order dependence of [Ce⁴⁺] and the fractional order of [alcohol] and [Ru³⁺] which was observed in the present study.

The authors wish to thank Prof. T. Navaneeth Rao and Dr. B. Sethuram for helpful discussions and Prof. M. M. Taqui Khan for providing laboratory facilities.

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SYNTHESIS OF THIOBENZOPHENE

A simple reaction between benzophenone and fenthion
[0, 0-dimethyl-0-(4-methylmercapto-3-methylphenyl)-thiophosphate] has been reported by the authors
earlier. It was observed that benzophenone at its
melting point reacts with fenthion to form thiobenzophene according to the reaction:

\[
\begin{align*}
& H_2CS \quad OCH_3 \quad CH_3 \quad OCH_3 \quad CH_3 \\
& \quad (I) \quad (II) \quad (III) \quad (IV)
\end{align*}
\]

We have now found that not only fenthion but all
the thiophosphates containing P = S give this reac-
tion. The organothiophosphates responding to this

reaction are listed in Table I. The above results are
confirmed by UV and mass spectrometric data.

The TLC studies of the reaction products of the
compounds in Table I and benzophene showed
blue spots having same Rf (0.69), suggesting thereby
the formation of thiohexanone with all the
organothiophosphates insecticides having P = S moiety.

UV and visible spectra of the blue compound (Fig. 1)
are similar to those reported by Brocklehurst and
Burawoy³. GC-Mass (Fig. 2) fragmentation further
confirms that the final product is thiohexanone.

\[
\begin{align*}
& S = Sumithion, P = Parathion, M = Malathion. \\
& \text{Fig. 1. UV and visible spectra of Thiohexanone as reaction product.}
\end{align*}
\]

\[
\begin{align*}
& \text{Intensity} \\
& \begin{array}{cccc}
& 500 & 600 & 700 & 800 \\
& 500 & 100 & 150 & 200 \\
& 50 & 100 & 150 & 200 \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
& \text{Temperature} \\
& \begin{array}{cccc}
& 50 & 100 & 150 & 200 \\
& 50 & 100 & 150 & 200 \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
& \text{Fig. 2. GC-MASS of reaction product.}
\end{align*}
\]
### Table 1

**Organothiophosphates reacting with benzophenone to form Thiobenzophenone**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction Product</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methathion</td>
<td>N, N-Dimethyl S-bis (carboxyloxyethyl) phosphorodithioate</td>
<td>(CH₃O)₂P(S)₂, CHCOOC₂H₅</td>
</tr>
<tr>
<td>Parathion</td>
<td>N, N-Diethyl phosphorothioate</td>
<td>(C₂H₅O)₂P(S)₂NO₂</td>
</tr>
<tr>
<td>Methyl Parathion</td>
<td>N, N-Dimethyl-0-(3-methyl-4-nitrophenoxy) phosphorothioate</td>
<td>(CH₃O)₂P(S)₂NO₂</td>
</tr>
<tr>
<td>Sumithion</td>
<td>N, N-Dimethyl-0-(3-methyl-4-nitrophenoxy) phosphorothioate</td>
<td>(CH₃O)₂P(S)₂NO₂</td>
</tr>
<tr>
<td>Fenthion</td>
<td>N, N-Dimethyl-0-(4-methylmercapto) 3-methylphenyl thiophosphate</td>
<td>(CH₃O)₂P(S)₂SCH₃</td>
</tr>
<tr>
<td>Fenathoate</td>
<td>N, N-Dimethyl-0-(4-ethoxy carbonyl benzyl) phosphorodithioate</td>
<td>(CH₃O)₂P(S)₂OOC₂H₅</td>
</tr>
<tr>
<td>Phorate</td>
<td>N, N-Diethyl-0-(ethyl thiomethyl) phosphorothioate</td>
<td>(C₂H₅O)₂P(S)₂SCH₂SC₂H₅</td>
</tr>
<tr>
<td>Fensulphothion</td>
<td>N, N-Diethyl-0-(4-methyl sulfinyl phenyl) monophosphorothioate</td>
<td>(C₂H₅O)₂P(S)₂SCH₂SC₂H₅</td>
</tr>
<tr>
<td>Demeton-S</td>
<td>N, N-Diethyl-0-(ethylthio) 2 (ethylthio)ethyl phosphorothioate</td>
<td>(C₂H₅O)₂P(S)₂SCH₂SC₂H₅</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>N, N-Dimethyl-0-(N,N-dimethylamino) methyl phosphorothioate</td>
<td>(CH₃O)₂P(S)₂SCH₂C(O)NHCH₃</td>
</tr>
</tbody>
</table>

The following compounds do not give this reaction with benzophenone under the experimental conditions, which shows that the proposed reaction is specific to the compounds containing P = S moiety.


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**Magnetic and Spectral Studies on Oxovanadium(IV) Complexes with Bidentate o-Pyridyl Thiosemicarbazide**

**Introduction**

Recently, in connection with our interest in the stereochmical studies on metal complexes with heterocyclic thiosemicarbazide and its substituted thiosemicarbazones. We report in this investigation, some penta-coordinated oxovanadium (IV) complexes with recently synthesised o-pyridyl thiosemicarbazide (C₈H₈N₄S, abbreviated as 'APT'). All are characterized by chemical analysis, magnetic and spectral (reflectance and i.r.) measurements in order to evaluate their stereochemistry.

**Experimental**

*Bis-mono-(chloro)cyano(hydroxo)-(APT) oxovanadium (IV) dichloride/dicyanide/mono-hydrate*: A bluish-red