enabling CAN to abstract selectively an electron, resulting in the formation of a cation-radical.

Curiously, a plot of $\log \left( \frac{k}{k_0} \right)_{\text{Ce}^{IV}}$ versus $\log \left( \frac{k}{k_0} \right)_{\text{V(V)}}$ at $65^\circ$ gives a very good correlation, indicating similar transition state in both the oxidation series.

One of the authors (S.N.) thanks the CSIR, New Delhi, for financial assistance.

References

Effect of Structure on Activation Parameters
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Received 28 July 1976; revised 11 October 1976; accepted 3 December 1976

The effect of substituents on the activation parameters has been discussed. The trend observed is explained on the basis of energies of the ground state and activated complex.

In the oxidation of fluorenes by ammonium metavanadate, a good linear free energy relationship as evidenced by a satisfactory Hammett plot was obtained. But a plot of $\Delta H^1$ and $\Delta S^1$ (the isokinetic plot) showed a marked deviation for the 2-nitrofluorene molecule. In view of a recent communication on the nature of variations of $\Delta H^1$ and $\Delta S^1$ with $\sigma$, we have analyzed our results in a similar fashion and the results are reported in this note.

The rate constants for the V(V) oxidation of the 2-substituted fluorenes and the derived activation parameters are presented in Tables 1 and 2.

The enthalpy of activation of the reaction increases with decrease in the electron density at the reaction centre as revealed by $\sigma$ values of the 2-substituents. These data do not have a linear

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Substrate & $h_0 \times 10^2$ (litre mole$^{-1}$ sec$^{-1}$) at & 50$^\circ$ & 57.5$^\circ$ & 65$^\circ$ \\
\hline
1-Methylfluorene & 2.98 & 4.98 & 9.97 \\
Fluorene & 2.38 & 4.26 & 8.02 \\
2-Iodofluorene & 0.88 & 1.57 & 3.21 \\
2-Chlorofluorene & 0.33 & 0.74 & 1.56 \\
2-Bromofluorene & 0.39 & 0.75 & 1.65 \\
2-Nitrofluorene & 0.017 & 0.038 & 0.077 \\
2-Ethylfluorene & 74.12 & 46.00* & 27.23† \\
\hline
\end{tabular}
\caption{Temperature Dependence of the Rate Constants}
\end{table}

*At 40$^\circ$. †At 30$^\circ$. 

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\hline
\end{tabular}
\caption{Temperature Dependence of the Rate Constants}
\end{table}
Table 2 — Activation Parameters for the Oxidation of Substituted Fluorenes by Ammonium Metavanadate

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$E_a$</th>
<th>$\Delta H^\ddagger$</th>
<th>$-T\Delta S^\ddagger$</th>
<th>$\Delta G^\ddagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal</td>
<td>kcal</td>
<td>kcal</td>
<td>kcal</td>
</tr>
<tr>
<td>2-Ethylfluorene</td>
<td>10.23</td>
<td>9.58</td>
<td>9.04</td>
<td>18.62</td>
</tr>
<tr>
<td>1-Methylfluorene</td>
<td>16.38</td>
<td>15.73</td>
<td>4.99</td>
<td>21.28</td>
</tr>
<tr>
<td>Fluorene</td>
<td>16.57</td>
<td>15.92</td>
<td>5.55</td>
<td>21.47</td>
</tr>
<tr>
<td>2-Iodofluorene</td>
<td>18.96</td>
<td>18.31</td>
<td>3.20</td>
<td>21.51</td>
</tr>
<tr>
<td>2-Bromofluorene</td>
<td>20.42</td>
<td>19.77</td>
<td>2.27</td>
<td>22.04</td>
</tr>
<tr>
<td>2-Chlorofluorene</td>
<td>21.05</td>
<td>20.40</td>
<td>1.75</td>
<td>22.15</td>
</tr>
<tr>
<td>2-Nitrofluorene</td>
<td>21.93</td>
<td>21.28</td>
<td>3.29</td>
<td>24.57</td>
</tr>
</tbody>
</table>

relationship, but tend to fall on the branches of a hyperbola (Fig. 1A) correlated by expression (1).

$$\Delta H^\ddagger = 26.8 \left[ \sigma_p + 0.4776 \right] \left[ \sigma_p + 0.8042 \right]$$  \hspace{1cm} \ldots (1)

It is curious that $T\Delta S^\ddagger$ also varies in a similar fashion with $\sigma_p$ (Fig. 1B). The curve is best represented by the hyperbola correlated by expression (2).

$$T\Delta S^\ddagger = -5.0176\sigma_p - 21.469 + 26.8 \left[ \sigma_p + 0.4776 \right] \left[ \sigma_p + 0.8042 \right]$$  \hspace{1cm} \ldots (2)

(at 323°K)

However, it is interesting to note that $\Delta G^\ddagger$ varies linearly with $\sigma_p$ (Fig. 1C). The fact that $\Delta G^\ddagger$ is a linear function of $\sigma$ and $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ are not, indicates that a common function between $T\Delta S^\ddagger$ and $\Delta H^\ddagger$ exists, i.e.

$$\Delta H^\ddagger = A_1\sigma + B_1 + f(\sigma)$$  \hspace{1cm} \ldots (3)

$$T\Delta S^\ddagger = A_2\sigma + B_2 + f(\sigma)$$  \hspace{1cm} \ldots (4)

Since $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ a linear relationship between $\Delta G^\ddagger$ and $\sigma$ can be derived, which is of the form

$$\Delta G^\ddagger = 5.0176\sigma_p + 21.469$$  \hspace{1cm} \ldots (5)

This is in good agreement with the least square analysis of $\Delta G^\ddagger_{\text{calc}}$ given by Eq. (6).

$$\Delta G^\ddagger_{\text{calc}} = 5.126 \sigma_p + 20.808$$  \hspace{1cm} \ldots (6)

Fig. 1D represents the curve for the plot of $\Delta H_{\text{calc}}$ and $T\Delta S_{\text{calc}}$ from Eqs. (1) and (2). This curve accounts for the experimental points.

The theoretical curves from expressions (1) and (2) are in excellent agreement with the rate data. This indicates that the empirical relationships for $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ are valid for the substituted fluorenes studied. Thus the nonlinear variation of $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ with $\sigma_p$ explains the observed deviation in the isokinetic plot. Also, the existence of a common function between $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ indicates a linear variation of $\Delta G^\ddagger$ with $\sigma_p$ which is actually obtained.

It is interesting to study the variation of $\Delta H^\ddagger$ versus $\sigma_p$ and $T\Delta S^\ddagger$ versus $\sigma_p$ obtained in the present case. The concave downward curve indicates that the enthalpy of activation increases with increasing $\sigma$. However, a steep decrease in $\Delta H^\ddagger$ is observed with electron releasing substituents. This can be explained by considering the energy of the ground state and the activated complex.

It is known that the methylene group in fluorene (I) can interact with the rings by hyperconjugation.

Such an interaction is facilitated by electron withdrawing groups in the 2-position, thus stabilizing the ground state of the molecule to a great extent. This increases, obviously, the enthalpy of activation. On the contrary, electron releasing groups at the 2-position destabilize the structure (II) by opposing the hyperconjugative effect. The ground state is therefore not stabilized. The activated complexes envisaged in the reaction is the cation radical of the type (III).

Hence the activated complex is stabilized by hyperconjugation both by the ethyl substituent and by the methylene group. This decreases largely the enthalpy of activation. An interesting extrapolation is the value of $\sigma_p$ when $\Delta H^\ddagger = 0$. When $\sigma_p = -0.4776$, $\Delta H^\ddagger$ becomes zero, and the reaction is instantaneous. Thus 2-methoxyfluorene reacts instantaneously under the experimental conditions.
The trend observed in $\Delta S^\ddagger$ versus $\sigma$ curve can be explained by considering the solvation of the activated complex. The activated complex is more polar in the case of 2-ethylfluorene resulting in a large decrease in entropy. The electron withdrawing substituents render the molecule a dipole resulting in the solvation of the ground state. Thus, a smaller change in $\Delta S^\ddagger$ is observed.

One of the authors (S.N.) thanks the CSIR, New Delhi for financial assistance.

References
3. de la Mare, P. B. D., Hall, D. M., Harris, M. M. & Hassan, M., Chewy Ind., (1958), 1086.

Oxopentafluoroniobates (V)
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Received 17 February 1976; accepted 16 September 1976

The oxopentafluoroniobates (V) of the type $[(CH_3)_4N]^+$ and $[M(py)_4]^+$, where $M = Cu$, Ni, Zn, Cd, Co and py = pyridine, have been prepared. The IR spectra and TGA data for the above compounds are reported.

A large number of oxopentafluoroniobates are known. In the present paper several new oxopentafluoroniobates of $(CH_3)_4N^+$ and $[M(py)_4]^+$, where $M = Cu$, Ni, Zn, Cd, Co, and py = pyridine, are reported. The compounds are studied through thermogravimetry and infrared spectroscopy.

Niobium pentoxide (purity about 99.9%) obtained from the sample was fumed with $H_2SO_4$ and then excess pyridine was added. The precipitate was filtered and then added to the niobium solution with stirring when immediately deep blue precipitate appeared.

The precipitate was filtered, washed with water, filter-pressed and dried in vacuo over fused $CaCl_2$; yield 7.3 g.

Light blue nickel compound was prepared as above starting from its carbonate (1.8 g). $Nb_2O_5$ (2 g), pyridine and HF; yield 6.6 g. The cadmium compound (white polyhedra) was obtained as above by adding a solution of tetrapyridinecadmium nitrate [prepared by dissolving cadmium carbonate (2.6 g) in minimum amount of $HNO_3$ (2N), and adding pyridine (5 g)] to a solution prepared by dissolving $Nb_2O_5$ (2 g) in HF (10%) and then neutralizing with pyridine. The zinc and cobalt compounds were prepared in a similar manner as the cadmium compound starting from their respective carbonates.

The analytical data are given in Table I. The above compounds hydrolyse in water with the generation of pyridine and are insoluble in common organic solvents.

The strong bands for Nb=O in the IR spectra were found to occur at 892-952, 918, 930-960, 935-958, and 918 cm$^{-1}$ for the Cu, Ni, Zn, Cd and Co compounds respectively. Thus it is observed that $\nu$Nb=O appears in the region, as observed in the case of $M^{11}NbOF_5$, $nH_2O$ ($M = Cu^{2+}$, Mn$^{2+}$, etc.). The data suggest that in the above tetrapyridine-metal compounds the $NbOF_5^-$ anion remains unaltered. Due to the limitations of the instrument bands below 700 cm$^{-1}$ could not be recorded.

### Table I — Analytical Data of Oxopentafluoroniobates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found (%)</th>
<th>Calc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M(II)</td>
<td>N</td>
</tr>
</tbody>
</table>