Stability of Ethylidene Radicals

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Previous attempts to study the ethylidene radical have involved the photolytic and thermal decomposition of diazoethane, CH\textsubscript{2}CHN\textsubscript{2}.\textsuperscript{1,2} The radical may also occur as an intermediate in the reactions of Na atoms with the asymmetrical dihalides of ethane,\textsuperscript{3,4} as well as in the photolysis and pyrolysis of acetaldehyde, CH\textsubscript{3}CH=N=N=CHCH\textsubscript{3}.\textsuperscript{5,6} We report here evidence for the existence of ethylidene in the photolysis of methyl ketene, CH\textsubscript{3}CH\textsubscript{2}CO.

Methyl ketene was prepared by the method of Jenkins,\textsuperscript{7} and purified by a slow bulb-to-bulb distillation, discarding the first fractions, one condensible in boiling CH\textsubscript{4}, and the other noncondensible. Hydrogenation of this latter subfraction showed it to be a mono-olefin, and its infrared spectrum showed the characteristic \(\nu\textsubscript{C=O}\) of ethylidene. The higher boiling subfraction could be further separated into two subfractions, one condensible in boiling CH\textsubscript{4}, and its infrared spectrum showed the \(\nu\textsubscript{C=O}\) of CO. The condensible fraction of the photolytic products to be a mono-olefin, and upon combustion proved to be a \(\text{C}_2\text{H}_4\). The noncondensible fraction, one condensible in boiling CH\textsubscript{4}, and the other noncondensible, on hydrogenation showed the \(\nu\textsubscript{C=O}\) of CO. The condensible fraction could be further separated into two subfractions, one condensible in boiling CH\textsubscript{4}, \((-161^\circ\text{C})\) the other noncondensible. Hydrogenation of this latter subfraction showed it to be a mono-olefin, and its infrared spectrum showed the 10.52 micron \(\nu\textsubscript{O=O}\) of ethylene. The higher boiling subfraction was also shown to be a mono-olefin by hydrogenation, and upon combustion proved to be a \(\text{C}_2\text{H}_4\). The amount of this fraction collected so far is so small as to preclude identification by infrared analysis, but it may be assumed to be a mixture of the butenes.

During the photolysis of pure methyl ketene, the pressure increased linearly with time up to about 15% decomposition. Beyond this point the slope decreased continuously, indicating an inhibitory action by one of the products. Addition of ethylene to the methyl ketene decreased the slope of the pressure-time curve (i.e., the manometric rate), indicating that it might be responsible for the effect observed at large percentage decomposition.

Measurements of the initial rate of production of \(\text{CO} / \text{C}_2\text{H}_4\), and \(\text{C}_2\text{H}_4\) as a function of initial pressure of methyl ketene were made. As seen in the Fig. 1, a plot of the \(\text{CO} / \text{C}_2\text{H}_4\) ratio as a function of initial methyl ketene pressure is a straight line with zero intercept. Similarly, a plot of the \(\text{C}_2\text{H}_4 / \text{C}_2\text{H}_4\) ratio as a function of the initial pressure is linear with a zero intercept. These data strongly support the following mechanism:

\[
\begin{align*}
\text{CH}_3\text{CH} &\rightarrow \text{CH}_2\text{CO} + \text{CO} \\
\text{CH}_3\text{CH}_2\text{CH} &\rightarrow \text{CH}_2\text{CH} - \text{CO} \\
\text{CH}_3\text{CH} &\rightarrow \text{CH}_2\text{CH} + \text{CO}
\end{align*}
\]

A steady-state treatment yields for the ratio of the rate of CO production to \(\text{C}_2\text{H}_4\) production \(\text{CO} / \text{C}_2\text{H}_4 = 1 + 2k_2P / k_1\), and for the rate of \(\text{C}_2\text{H}_4\) production relative to \(\text{C}_2\text{H}_4\), production \(\text{C}_2\text{H}_4 / \text{C}_2\text{H}_4 = k_0P / k_1\). Thus we see that under the conditions of our experiments the rate of rearrangement of the ethylidene radical to ethylene is comparable to the rate of attack of ethylidene on methyl ketene.

The effects of temperature, inert gas, light intensity, and wavelength are being investigated and will be reported later.

\textsuperscript{1} F. J. Rice and A. L. Glaebrook, J. Am. Chem. Soc. 56, 741 (1934).
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Structure of Feather Keratin*

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Rather, in view of the observed maxima in $P(r)$, it appears most likely that the structure is based on extended polypeptide chains.

The model which we propose for the structure of feather keratin has the following features: (1) The fundamental unit is a helical extended polypeptide chain of pitch 190 A and radius 8.0 A. There are 64 amino acid residues in the 190 A repeat. (2) In the 190 A repeat there are 8 uniformly spaced proline residues. (3) Ten of these helices aggregate coaxially as a result of lateral hydrogen bonding between chains, the proline residues of neighboring chains packing together at about the same level. The polypeptide chains are in the parallel configuration and are about 4.85 A apart. The side chains project both into and out of the approximately cylindrical unit formed by the main chains. (4) Seven of these cylindrical units form a somewhat stable aggregate.

The percentage of proline required by the proposed model is in good agreement with that found. The model accounts fairly well for the strong equatorial and meridian reflections in the x-ray diffraction pattern, and in particular for the stable meridian reflection at 23.7 A, which arises from the axial repeat of the proline residues. Fair agreement with the equatorial intensities indicates that the proposed structure is a most likely one. The reflection at 23.7 A, which arises from the axial repeat of the cylindrical unit contains water. The structure predicts an infrared dichroism which is consistent with the observed value. Construc­ tion of molecular models, with particular reference to the configuration of the polypeptide chain near the proline residue, indicates that the proposed structure is a most likely one. The relatively homogeneous particles which are obtained when feather keratin is solubilized can be accounted for by the susceptibility to hydrolysis of certain of the peptide links adjacent to the proline residues. The apparent absence of end groups in soluble feather keratin is probably a consequence of the inadequacy of the dinitrifluorobenzene method when the terminal group is proline.

Linear Extrapolation of the Vibrational Energy Levels of Ionic Molecules

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In a comparison of the true values of the dissociation energies $D_0$ of diatomic molecules with those values obtained through linear extrapolation of vibrational energy levels, $D_{al}$, Gaydon found $D_0 < D_{al}$ for the ground electronic states of all non-ionically bound molecules except Cl₂ and CIF. The recent CIF data of Nielsen and Jones yielded a ratio $D_0/D_{1953} = 0.86$, and further strengthened the conviction that $D_0 < D_{al}$ for all non-ionic molecules. Gaydon's comparison of $D_0$ and $D_{al}$ for predominantly ionic molecules led to no such unification. In the case of ionic molecules it was expected that $D_0 > D_{al}$, and this was true for only six of the ten molecules with sufficient data for a comparison.

### Table I. $D_0/D_{al}$ for the halides of Al, Ga, In, and Tl.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Vibrational data reference</th>
<th>$D_0$ (in ev)</th>
<th>$D_0$ (in ev)</th>
<th>$D_0$ (in ev)</th>
<th>$D_0/D_{al}$</th>
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<tr>
<td>AlCl</td>
<td>a 47.2</td>
<td>6.7</td>
<td>9.1</td>
<td>2.2</td>
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<tr>
<td>AlBr</td>
<td>b 3.7</td>
<td>5.1</td>
<td>7.3</td>
<td>2.0</td>
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<tr>
<td>AlF</td>
<td>c 3.5</td>
<td>5.0</td>
<td>7.2</td>
<td>2.3</td>
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</tr>
<tr>
<td>GaCl</td>
<td>d 3.5</td>
<td>6.2</td>
<td>8.6</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>GaBr</td>
<td>e 3.1</td>
<td>6.0</td>
<td>8.6</td>
<td>1.4</td>
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</tr>
<tr>
<td>GaF</td>
<td>f 3.5</td>
<td>6.0</td>
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<tr>
<td>InCl</td>
<td>g 3.5</td>
<td>6.4</td>
<td>8.9</td>
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<tr>
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<td>8.9</td>
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* See reference 13.