2. By studying oxidation in the presence of cumene hydroperoxide it has been possible
to determine rate constants for double-bond addition of cumene peroxide radicals in acrylic
and methacrylic esters of polyhydric alcohols. The reactivity of the double bond diminishes
as the number of ethereal groups in the molecule is increased, possibly because of multi-
dipole interaction in the initial and transition states.

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THERMODYNAMIC AND QUANTUM-CHEMICAL ESTIMATES OF THE CONJU GATION ENERGY IN SIMPLE VINYL ETHERS

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Since the basic properties of the vinyl ethers are determined by \( p-\pi \) conjugation, these
compounds are particularly suited for studies on conjugation effects of this type [1]. The
present work was an attempt to measure the conjugation energy in ethers of the \( \text{CH}_2=\text{CHOR} (R = \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7, \text{i-C}_3\text{H}_7, \text{C}_2\text{H}_4\text{Cl}, \text{CH}==\text{CH}_2, \text{C}_6\text{H}_5) \) series. This involved measurement of the
heats of combustion of various ethers, followed by calculation of their heats of formation
from the elements in their standard states (\( \Delta H_f^\circ \)). The energy of \( p-\pi \) 0-atom conjugation with
a double bond was determined as the difference between the measured and calculated \( \Delta H_f^\circ \) values
(Tables 1). The latter values were obtained from sums of the form \( \Delta H_{\text{calc}} = \Delta H_{\text{ad}} + \Delta H_{\text{ind}} \). The value of \( \Delta H_{\text{ad}} \), the additive component in such sum, was calculated from the expression
\( \Delta H_{\text{ad}} = \sum n_i \Delta H_i \), where \( n_i \) is the number of groups of the i-th type, and \( \Delta H_i \) is the additive contribution
of each such group [3].

The value of \( \Delta H_{\text{ind}} \), the inductive component of the equation, was obtained from the mutual polarization of the RO and \( \text{CH}_2=\text{CH} \) groups, working through the expression

\[ \Delta H_{\text{ind}} = \alpha \sum n_i \sigma_0 \sigma_i \sigma^* \]

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from Table 1. Formation Ethalpies and Conjugation Energies for Certain CH_2=CHOR Vinyl Ethers (kcal/mole)

<table>
<thead>
<tr>
<th>R</th>
<th>( \Delta H_f^0 ) (exp., gas)</th>
<th>( \Delta H_f^0 )</th>
<th>( \Delta E_{\mu\nu} )</th>
<th>R</th>
<th>( \Delta H_f^0 ) (exp., gas)</th>
<th>( \Delta H_f^0 )</th>
<th>( \Delta E_{\mu\nu} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_2H_5 )</td>
<td>-33.6±0.2 [2]</td>
<td>-6.8</td>
<td>-6.7</td>
<td>( C_2H_5Cl )</td>
<td>-40.6±0.9</td>
<td>-7.3</td>
<td>-6.6</td>
</tr>
<tr>
<td>( n-C_3H_7 )</td>
<td>-36.6±0.5</td>
<td>-6.8</td>
<td>-6.7</td>
<td>( n-C_4H_9 )</td>
<td>-5.6±0.5</td>
<td>-5.6</td>
<td>-6.6</td>
</tr>
<tr>
<td>( i-C_4H_7 )</td>
<td>-35±0.5</td>
<td>-6.9</td>
<td>-6.9</td>
<td>( CH=CH_2 )</td>
<td>-3.3±0.3 [2]</td>
<td>-4.0</td>
<td>-4.1</td>
</tr>
<tr>
<td>( n-C_4H_9 )</td>
<td>-44±0.6</td>
<td>-7.3</td>
<td>-6.9</td>
<td>( CH=CH_2 )</td>
<td>-3.3±0.3 [2]</td>
<td>-4.0</td>
<td>-4.1</td>
</tr>
</tbody>
</table>

*Exact to within +1.2 kcal/mole.

where \( \alpha \), 2.3 kcal/mole, is the constant for inductive interaction in the gaseous state; 0.39 is the coefficient for propagation of inductive effects through the bridging C atom; \( n \) is the number of C atoms lying between the substituents; and \( \sigma_1^* \) and \( \sigma_2^* \) are the Taft inductive constants for the RO and CH=CH_2 groups [3].

The energy of \( p-\pi \) interaction in each compound was also calculated by MINDO/2 methods [4]; here we followed [5] and fixed our attention on the \( E_{\mu\nu} \) component of \( E_{AB} \), the energy of interatomic interaction [6] [\( \mu \) designates the \( p_\mu \) component of the oxygen (atom A) AO and \( \nu \) the \( p_\nu \) component of the \( \alpha \) or \( \beta \) carbon (atom B) AO, and the double bond is assumed to lie in the XY plane]. If the energy required for a 90° rotation of the radical around the C_sp2-O bond is taken to be zero, the value of \( \Delta E_{\mu\nu} \), the energy of \( p-\pi \) interaction, is given as the difference of values corresponding to \( \Phi = 0^\circ \) (trans form) and \( \Phi = 90^\circ \) (cf. Table 1).

The fact that the values of \( \Delta H_f^0 \) and \( \Delta E_{\mu\nu} \) were in close agreement was taken as an indication that the approach adopted here was correct, at least insofar as it applies to the vinyl ethers.

The attempt was also made to estimate the effect of the benzene ring on the conjugation energy in the vinyl oxy group (vinyl phenyl ether) by calculating the group conjugation energy, first at \( \Phi = 0^\circ \) and then at 90° ring rotation.

The fact that the variation in \( E_{\mu\nu} \) was only of the order of 2.8 kcal/mole was taken as an indication that conjugation is weak in the vinyl oxy group, just as suggested by the earlier work of [7]. The thermodynamic value of the total energy of \( p-\pi \) interaction in vinyl phenyl ether was 6.6 kcal/mole. Rotation of one of the vinyl oxy groups of divinyl ether by an angle of 90° around the C-O bond reduced the value of \( E_{\mu\nu} \) by 7 kcal/mole. At the same time, the value of \( E_{\mu\nu} \) for the second bond was increased by 0.8 kcal/mole. This seems to be a characteristic value for \( p-\pi \) conjugation weakening in the vinyl oxy group. In each vinyl oxy group the total \( \Delta E_{\mu\nu} \) was 6.2 kcal/mole.

Thus, the presence of two \( \pi \) systems at the heteroatom tends to weaken the conjugation of this atom with each system individually. This conclusion is consistent with the discussion of \( \pi \)-electron system competition presented in [8].

**EXPERIMENTAL**

The purity of the various vinyl ethers was checked by cryoscopic and gas-liquid chromatographic methods [9]. Combustion of four of the ethers was carried out in a stationary bomb calorimeter equipped with an isothermal shield. The heat of combustion is the energy change associated with the reaction

\[
C_aH_bO_c(l) + \left( \frac{a + \frac{b}{4} - \frac{c}{2}}{4} \right) O_{2(g)} = aCO_{2(g)} + \frac{b}{2}H_2O(l)
\]

The heat of combustion of vinyl \( \beta \)-chloroethyl ether was determined with a platinum-lined, rotating bomb calorimeter. The bomb load included 15 cm³ of a 0.37 N arsenous anhydride solution to reduce the final products resulting from the combustion of gaseous chlorine and chloride ions. The \( O_2 \) pressure in the bomb was 3 MPa. Mineral oil served as an auxiliary substance. The heat of combustion of the vinyl \( \beta \)-chloroethyl ether is the energy liberated in the following standard state reaction:

\[
C_2H_5OCl(l) + 5.5 O_{2(g)} + 600 H_2O(l) = 4CO_{2(g)} + 3.5 H_2O(l) + HCl + 600 H_2O(sol)
\]

The thermal constants of the calorimeter were determined through the combustion of standard benzoic acid, the heat of combustion of the acid under the calibrating conditions being taken

538