The second signal, at 6 3.30 ppm, corresponds to the natural spectrum of pyridoxol hydrochloride (in deuteriomethanol). After incubation with the deuterium spectra (B and D) more than incorporation of deuterium is stereochemically controlled.

It is of interest that deoxyxylulose, which is now shown to be implicated in the biosynthesis of vitamin B₆ in E. coli, also serves as a precursor of the thiazole unit of vitamin B₆ in the same organism and that a D-1-deoxypentulose has been postulated as an intermediate of the biosynthesis of vitamin B₃.

Acknowledgment. This work was supported by grants from the Medical Research Council of Canada (to R.E.H.) and the Natural Sciences and Engineering Research Council of Canada (to I.D.S.). We thank Dr. Tomasz Kozluk for the preparation of the deuterium-labeled samples of D- and L-1-deoxyxylulose and Richard Pauloski for skilled technical assistance.

Electron-Transfer Reactions in the Marcus Inverted Region. Charge Recombination versus Charge Shift Reactions

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The recent experimental verification of the Marcus inverted region has stimulated renewed theoretical interest in electron-transfer processes. Kakitani and Mataga have described a model in which partial solvent dielectric saturation of ionic species involved in electron-transfer reactions results in a negligible decrease in rate in the inverted region for reactions in which two neutral species yield two ion species (termed charge separation reactions, CS). The model also predicts a pronounced inverted region for charge recombination reactions (CR) in which two ions yield two neutral species and intermediate behavior for charge shift (CSH)
chloride at 25 °C.

solution in a polar solvent.

table were determined by using both the transient absorption and photoacoustic calorimetry. The results (Table I) demonstrate that the two techniques give very similar results, despite the fact that each uses different actinometers.

Table I. Quantum Yields for Free Radical Ion Formation from N-Methylacridinium Radical/Alkylbenzene Radical Cation Pairs in Acetonitrile at 25 °C.

<table>
<thead>
<tr>
<th>alkylbenzene</th>
<th>ΔGret</th>
<th>Ψprog</th>
<th>Ψsep</th>
<th>kret/ksep</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-xylene</td>
<td>-2.59</td>
<td>0.27</td>
<td>0.26</td>
<td>2.7</td>
</tr>
<tr>
<td>o-xylene</td>
<td>-2.59</td>
<td>0.27</td>
<td>0.28</td>
<td>2.7</td>
</tr>
<tr>
<td>mesitylene</td>
<td>-2.56</td>
<td>0.19</td>
<td>0.15</td>
<td>4.3</td>
</tr>
<tr>
<td>p-xylene</td>
<td>-2.51</td>
<td>0.16</td>
<td>0.14</td>
<td>5.4</td>
</tr>
<tr>
<td>1,2,3-trimethylbenzene</td>
<td>-2.37</td>
<td>0.084</td>
<td>0.08</td>
<td>10.9</td>
</tr>
<tr>
<td>1,2,3,4-tetramethylbenzene</td>
<td>-2.29</td>
<td>0.054</td>
<td>0.05</td>
<td>17.7</td>
</tr>
<tr>
<td>1,2,3,5-tetramethylbenzene</td>
<td>-2.29</td>
<td>0.049</td>
<td>0.049</td>
<td>19.6</td>
</tr>
<tr>
<td>1,4-dimethyltetrahydrophenanthrene</td>
<td>-2.26</td>
<td>0.051</td>
<td>0.051</td>
<td>18.8</td>
</tr>
<tr>
<td>naphthalene</td>
<td>-2.23</td>
<td>0.042</td>
<td>0.05</td>
<td>22.8</td>
</tr>
<tr>
<td>octahydrophenanthrene</td>
<td>-2.22</td>
<td>0.044</td>
<td>0.044</td>
<td>21.7</td>
</tr>
<tr>
<td>octahydroantranecene</td>
<td>-2.17</td>
<td>0.039</td>
<td>0.039</td>
<td>24.7</td>
</tr>
<tr>
<td>pentamethylbenzene</td>
<td>-2.16</td>
<td>0.037</td>
<td>0.037</td>
<td>26.0</td>
</tr>
<tr>
<td>hexamethylbenzene</td>
<td>-2.04</td>
<td>0.031</td>
<td>0.031</td>
<td>31.3</td>
</tr>
</tbody>
</table>

---

*Quantum yield measured using transient absorption spectroscopy.

†Quantum yield measured using pulsed photoacoustic calorimetry.

‡Calculated from Ψprog using eq 1.

---

Figure 1. The ratio of the rates of return electron transfer and separation (kret/ksep) for (A) the charge recombination (CR) reaction between cyanoanthracene radical anions and alkylbenzene radical cations and (B) the charge shift (CSH) reaction between N-methylacridinium radicals and alkylbenzene radical cations, as a function of the electron-transfer reaction free energy (ΔGret) in acetonitrile at 25 °C.

and photoacoustic methods. The results (Table I) demonstrate that the two techniques give very similar results, despite the fact that each uses different actinometers. The quantum yields are related to ksep and kret as shown in eq 2. Although the separation rate is expected to be higher in the case of the acridinum acceptor, since there is no coulombic attraction to overcome in the radical/cation pair as in the anion/cation pair, this rate is likely to be constant within each set of data. Changes in the quantum yields, therefore, are due to changes in the rates of return electron transfer, which decrease as the exothermicity of the reaction increases, i.e., ΔGret decreases. ΔGret is given by the negative of the energy stored in the ion pair, Eprog(donor) - Eprog(acceptor). In Figure 1 are plotted the rate ratios kret/ksep for both the CR and CSH reactions, as a function of ΔGret.

The data can be analyzed as before using a semiclassical theory of electron-transfer reactions, where the reaction rate is described as the product of a relative Franck-Condon factor (FC)

\[
k_{\text{et}} = k_0 \exp(-\frac{\Delta G_{\text{et}}}{k_B T})
\]

\[
P = (\pi / h^2 \lambda k_B T)^{1/2} |V|^2 / k_{\text{et}}
\]

(7) The photoacoustic apparatus has been described previously. The Ψprog were determined by using the equation, Ψprog = (1 - Ψprog)Epro/ΔG, in which Ψprog is the fluorescence quantum yield, α is the fraction of the photon energy released as heat in the reaction, Epro is the photon energy, and ΔG is the energy of the radical ions, given by Eprog(donor) - Eprog(acceptor). Experimental waveforms were obtained from photolysis (410 nm, 69.8 kcal/mol) of argon-degassed, acetonitrile solutions containing MA⁺ (OD > 0.3-0.7) and the substituted benzenes (0.2 M). Analysis using calibration waveforms obtained from photolysis of similar solutions containing ferrocene gave the experimental values. Experiments were also performed with added 4,4'-dimethoxytoluene (DMS, 1 × 10⁻⁵ M) which results in secondary electron transfer from DMS to the radical anion of the substituted benzenes. By using this method, knowledge of the absolute energies of each of the geminate pairs is not necessary. Both methods gave similar Ψprog values. Averages of the values obtained by using the two methods are given in Table I.

(8) The two techniques also gave similar quantum yields for Ψprog from the A⁻⁰/D⁺⁺ pairs (eq 1a).

(9) Van Duyne, R. P.; Fischer, S. E. Chem. Phys. 1974, 5, 137.

dependence of the rate ratio on scaling parameter that includes the separation rate squared respectively, are appropriate for both sets of data? The fitting value of of the rearranged vibrational modes.

It is clear from Figure 1 that both sets of data can be described very well by the same semiclassical formalism in which the effects of solvent dielectric saturation are not included. Indeed, in the procedure thus involves finding the best values for $P$ and $A$. The due to the somewhat smaller $A$ for the CSH reaction. Thus, the $A$ of 0.3 eV, Figure I) the decrease in rate with increasing exothermicity CR reaction, although the fitting procedure reveals that this is not predicted for the CSH reaction if both MA$^-$ and the MA radical were to be predicted for the CSH reaction.

Additions

James F. Blake, Scott G. Wierschke, and
William L. Jorgensen*

Department of Chemistry, Purdue University

Received September 2, 1988

According to conventional transition state theory, the transition state for a reaction is located at the potential energy maximum along the minimum energy reaction path (MERP). However, this definition can lead to serious errors in computed rate constants. The most relevant point is actually the maximum in the free energy of activation curve or "variational transition state" (VTS). Many of the dynamical consequences of free energy of activation maxima have been studied for atom-transfer reactions using mostly semiempirical potential energy surfaces and a few ab initio surfaces. The reaction coordinate, $r_\text{c}$, is defined as the distance between the carbene carbon and the center of the CC bond in ethylene. A MERF was obtained by geometry optimizations in $C_2$ symmetry with the 6-31G(d) basis set at fixed values of $r_{\text{c}}$. Four stationary points (reactants, $\pi$-complex, transition state, and product) were located and confirmed by frequency calculations. The effect of electron correlation was then estimated by single-point calculations with MP2 theory in the frozen core approximation for each 6-31G(d) optimized geometry.

In view of the pronounced correlation effects, the stationary points were reoptimized including the correlation energy at the MP2(FULL)/6-31G(d) level on a Cray XMP. Frequency calculations were carried out for nine of the 6-31G(d) optimized points to compute the zero-point corrections, enthalpies, and entropies needed to construct the free energy of activation profile.

Potential Energy Surfaces (Cs)

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The work at the University of Rochester was supported by the National Science Foundation (CHE-871370). The authors thank R. A. Marcus for providing a preprint of his work and for valuable discussions.

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