Density functional study of fulminate anion-cyanate anion rearrangement

Sunita Rani & N K Ray*
Chemistry Department, University of Delhi,
Delhi 110 007, India

Received 2 January 1998

Density functional theory is used to study the rearrangement of fulminate anion to cyanate anion. The reaction is predicted to be exothermic. It is shown that reaction proceeds via an oxazirinyl anion intermediate. Our calculated results are in excellent agreement with the results of more elaborate high level post-SCF studies.

Only a few theoretical investigations have been made to study the rearrangement (Fig. 1) of fulminate anion (I) to cyanate anion (II). Holsber and Beck carried out INDO calculations without geometry optimization to conclude that the rearrangement proceeds via a stable oxazirinyl anion intermediate (III) which is separated by barriers of 63.2 and 88.8 kcal mol\(^{-1}\) from CNO\(^{-}\) and OCN\(^{-}\) respectively. Li et al. have shown the existence of an oxazirinyl intermediate which is separated by much lower barriers of 12.4 and 4.1 kcal mol\(^{-1}\) from CNO\(^{-}\) and OCN\(^{-}\) respectively. These authors have suggested only a fleeting existence of the intermediate. The wavefunctions for the transition state (V) involved in the reaction intermediate to OCN\(^{-}\) are found to be RHF-unstable. Very recently Cheung and Li have studied the isomerization of fulminate anion. These authors have noted that the wavefunctions for the intermediate (III) and transition state (V) are RHF-unstable for different levels of post-SCF methods. These authors have used BD (Brueckner theory with double excitation) and BD (T) (BD augmented with perturbative triple excitation) for geometry optimization and they have shown that at this level of theory the wavefunctions for (V) are RHF-stable. In the present work our objective is to examine the adequacy of density functional method to study the isomerization of fulminate anion.

Computational details

The density functional (DF) studies were made using two different functionals: (i) Becke’s three-parameter exchange with Lee, Yang and Parr’s correlation functional (i.e. B3LYP) and (ii) Becke’s three-parameter exchange with Perdew and Wang’s correlation functional (i.e. B3PW91).

The geometries were optimized by means of analytical gradients. Harmonic vibrational frequencies were calculated using analytical second derivatives. 6-31+G(d) basis set was used for all calculations reported here. All stationary points were characterized by examining the number of imaginary frequencies and the eigenvalues of the Hessian matrix. GAUSSIAN 94 quantum chemistry package was used for all calculations reported here.

Result and discussion

It is worthwhile to point out that all wavefunctions used here are found to be RHF-stable. Our opt-
Table 1 – Calculated equilibrium geometries and some selected bond orders

<table>
<thead>
<tr>
<th>System</th>
<th>Parameter</th>
<th>Bond order</th>
<th>Present</th>
<th>Results Lit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNO⁻ (linear)</td>
<td>C-N</td>
<td>1.180 (1.157)</td>
<td>1.188 (1.188)</td>
<td>1.196</td>
</tr>
<tr>
<td></td>
<td>N-O</td>
<td>0.906 (0.880)</td>
<td>0.906 (0.870)</td>
<td>0.929</td>
</tr>
<tr>
<td>(IV)</td>
<td>C-N</td>
<td>0.828 (0.818)</td>
<td>0.828 (0.818)</td>
<td>0.840</td>
</tr>
<tr>
<td>Intermediate</td>
<td>N-O</td>
<td>1.453 (1.479)</td>
<td>1.453 (1.479)</td>
<td>1.457</td>
</tr>
<tr>
<td>(III)</td>
<td>&lt;O-N-C</td>
<td>100.2 (99.6)</td>
<td>100.2 (99.6)</td>
<td>100.2</td>
</tr>
<tr>
<td>(V)</td>
<td>N-O</td>
<td>1.269 (1.263)</td>
<td>1.269 (1.263)</td>
<td>1.275</td>
</tr>
<tr>
<td></td>
<td>&lt;O-N-C</td>
<td>1.619 (1.642)</td>
<td>1.619 (1.642)</td>
<td>1.671</td>
</tr>
<tr>
<td>OCN⁻ (linear)</td>
<td>C-N</td>
<td>1.205</td>
<td>1.205</td>
<td>1.205</td>
</tr>
<tr>
<td></td>
<td>C-O</td>
<td>1.243</td>
<td>1.243</td>
<td>1.243</td>
</tr>
</tbody>
</table>

with the results of Cheung and Li³. The following points emerge from the present study:

(i) DF methods like B3PW91 and B3LYP lead to RHF-stable wavefunctions for all systems studied here.

(ii) The predicted barrier heights and exothermicity of the reaction are in excellent agreement with the results of computationally more expensive post-SCF methods.

Acknowledgement

One of the authors (SR) is thankful to the UGC, New Delhi for the award of Senior Research Fellowship.

References