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Abstract

The enol-keto tautomerism in radical cations has been considered to involve a symmetry-forbidden 1,3-hydrogen shift. An alternative process involves two consecutive 1,2-hydrogen shifts. The $\Delta H_f$'s of the intermediate ions formed by a 1,2-hydrogen shift in the radical cations of phenol and the enol form of acetic acid have been calculated to be 220 and 191 kcal/mol, respectively. These $\Delta H_f$'s indicate barriers to the keto-enol tautomerism via two consecutive 1,2-hydrogen shifts of 50 and 47 kcal/mol, respectively, in good agreement with previously determined experimental values of 55 and 51 ± 10 kcal/mol, respectively. Estimations of transition state energies for the tautomerism via two consecutive 1,2-hydrogen shifts in the closed shell systems, vinyl alcohol ≡acetaldehyde, $\text{H}_2\text{C}≡\text{CH}_3$ ≡H₃C≡CH₂, and $\text{CH}_3\text{CH}=\overset{\text{O}}{\text{CH}}_3$ ≡CH₃CH₂≡CH₂, indicate that the assumption of a symmetry-forbidden 1,3-hydrogen shift is not required.
On the Mechanism of the Keto-Enol Tautomerism in Radical Cations and Gas Phase Closed Shell Systems

Sir:

Recently, a maximum barrier of 2.4 eV (55.2 kcal/mol) was determined\(^1\) for the enol-keto tautomerism of the metastable phenol radical cation (1)\(^2\) to the 2,4-cyclohexadien-1-one radical cation (3).\(^5\) This tautomerism was considered to be a specific example of a sigmatropic 1,3-hydrogen migration, a symmetry-forbidden process.\(^1\)

We propose that the energetics of this reaction may be accounted for by two consecutive 1,2-hydrogen shifts.\(^9\) The first 1,2-hydrogen shift would give

\[
\begin{align*}
\text{OH}^+ & \quad \text{CH}^+ \\
\begin{array}{c}
\text{H} \\
\end{array} & \quad \begin{array}{c}
\text{H} \\
\end{array} \\
\text{O} & \quad \text{C} \\
\end{align*}
\]

\(\Delta H_f^\circ \approx 170 \text{ kcal/mol} \quad \Delta H_f^\circ \approx 220 \text{ kcal/mol} \quad \Delta H_f^\circ \approx 188 \text{ kcal/mol} \)

ion 2 which should approximate the energy of the transition state in the enol-keto tautomerism by this mechanism.

The \(\Delta H_f^\circ\) of ion 2 may be estimated from the proton affinity of benzene,\(^10\) which gives a \(\Delta H_f^\circ\) for cyclohexadienylum of 205.4 kcal/mol. The \(\Delta H_f^\circ\) of 2,4-cyclohexadien-1-yl is 50 kcal/mol,\(^11\) and thus the ionization potential (IP) of this radical is 155.4 kcal (6.76 eV). A ring correction value of -1.5 kcal/mol
should be used in order to calculate the $\Delta H_f$ of 2,4-cyclohexadien-1-yl by the
additivity procedure. $^6$ The $\Delta H_f$ of the diradical corresponding to ion 2
can now be calculated to be 64.1 kcal/mol according to the additivity procedure $^6$
using a group additivity value of 9.4 kcal/mol for C-(O) (C) (Cd) (H) and
C-(O) (O) (Cd) (H), which was derived from the value of 7.8 kcal/mol for
C-(O) (C)$_2$ (H) plus the difference between the value of -7.2 kcal/mol for
C-(H) (O) (C)$_2$ and -5.6 kcal/mol for C-(H) (O) (C) (Cd) $^{12}$. Assuming no orbital
overlap between the radical and cation orbitals in ion 2, the IP of the diradical
should be similar to the IP of 2,4-cyclohexadien-1-yl giving a $\Delta H_f$ for ion,
2 of 220 kcal/mol.

The difference in the $\Delta H_f$ of ions 1 and 2 represents an activation
energy of 50 kcal/mol for the enol-keto tautomerism of ion 1 in good
agreement with the experimental value of 55 kcal/mol. $^1$

The barrier to the enol-keto tautomerism of the ionized enol form of
acetic acid to ionized acetic acid has been found to be $\sim$51 kcal/mol. $^{13}$
Although the $\Delta H_f$ of the intermediate formed, $^+CH_2CH(OH)0^+$, if the tautomerism
occurred via successive 1,2-H shifts was estimated to be 205 kcal/mol $^{13}$ by

$$
\begin{align*}
H_2C-C(OH) & \xrightleftharpoons[1,2-H]^{\text{shift}} H_2C=CH(OH) & \xrightleftharpoons[1,2-H]^{\text{shift}} CH_3COH \\
\Delta H_f & 144 \text{ kcal/mol} & \Delta H_f & 191 \text{ kcal/mol} & \Delta H_f & 136 \text{ kcal/mol}
\end{align*}
$$

Franklin's group equivalents, this pathway was considered unlikely because
the estimated $\Delta H_f$ of the intermediate ion was 10 kcal/mol greater than the
experimental transition state energy of 195 $\pm$ 10 kcal/mol. An estimation
of -3.4 kcal/mol using group additivity values\textsuperscript{6,14} for the $\Delta H_f$ of the diradical corresponding to this intermediate ion and an estimated IP of $\sim 8.45$ eV for this diradical similar to the IP of $\cdot \text{CH}_2\text{CH}_2\text{OH}$\textsuperscript{16} gives a value of 191 kcal/mol for the $\Delta H_f$ of the intermediate ion. This value indicates that the tautomerism via two successive 1,2-H shifts is energetically possible.

The estimated $\Delta H_f$'s of the intermediate ions in these two examples are lower than the experimental values by 4-5 kcal/mol. A possible inductive destabilizing effect of the oxygen radical was not included in the estimated $\Delta H_f$'s, but this effect would not be expected to be more than the inductive destabilizing effect of 2.6 kcal/mol for the hydroxyl group in HOCH$_2$CH$_2$\textsuperscript{16}.

The barrier to the enol-keto tautomerism of an isolated molecule of vinyl alcohol to acetaldehyde has been found by a recent \textit{ab initio} calculation to be $\sim 105$ kcal/mol for the symmetry-forbidden suprafacial 1,3-H shift and $\sim 85$ kcal/mol for the sterically unfavorable symmetry-allowed antarafacial 1,3-H shift (transition state energy levels of 77 and 57 kcal/mol, respectively).\textsuperscript{17} The energy of the transition state for the tautomerism via two successive 1,2-H shifts is estimated to be slightly higher than the transition state energy of 44.4 kcal/mol determined for the isomerization of ethylene oxide to acetaldehyde. The kinetics of this isomerization were attributed to the intermediacy of the diradical, $\cdot \text{CH}_2\text{CH}_2\text{O}$, $\Delta H_f$ (est) 41.9 kcal/mol, with an additional 2.5 kcal/mol for the 1,2-H shift.\textsuperscript{6} The energy for the 1,2-H shift leading to vinyl alcohol from the diradical intermediate may be as much as 10 kcal/mol, similar to the energy for
the 1,2-H shift from the diradical intermediate in the isomerization of cyclopropane to propylene.\textsuperscript{6} Thus the transition state energy for the vinyl alcohol-acetaldehyde tautomerism via two successive 1,2-H shifts is estimated to be $\sim$52 kcal/mol, lower than the transition state energy for the allowed but sterically unfavorable 1,3-H shift.

The barrier to tautomerism in another closed shell system has been found to be $\leq$83 kcal/mol for \( H_2C=O^+CH_3 \rightleftharpoons CH_3O^+CH_2 \)\textsuperscript{18} and $\geq$85 kcal/mol for \( CH_3CH=O^+CH_3 \rightleftharpoons CH_3CH_2O^+CH_2 \).\textsuperscript{18,19} The $\Delta H_f$ of the intermediate diradical \( CH_2\text{OHCH}_2^+ \), via two successive 1,2-H shifts in the first system was estimated to be 217 kcal/mol by the additivity procedure,\textsuperscript{22} 19 kcal/mol less than the experimental transition state energy\textsuperscript{18,19} which was considered to be an upper limit. A similar estimation for the $\Delta H_f$ of the diradical intermediate in the second system, \( CH_3\text{OHCH}_2^+ \), gave a value of 203 kcal/mol,\textsuperscript{23} 14 kcal/mol less than the experimental transition state energy.\textsuperscript{18,19} If the additional energy for the 1,2-H shift from the diradical is similar to that found for the 1,2-H shift from the diradical intermediate in the isomerization of cyclopropane to propylene,\textsuperscript{6} then the tautomerism via two successive 1,2-H shifts in these systems is in agreement with the experimental barriers and does not require the assumption of a symmetry-forbidden 1,3-H shift.\textsuperscript{24}

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The $\Delta H_f$ of 1 is the sum of the $\Delta H_f$ phenol ($-23.1$ kcal/mol)$^3$ and its adiabatic IP (8.4 eV)$^6$.


The $\Delta H_f$ of 2 is the sum of the $\Delta H_f$ of 2,4-cyclohexadien-1-one ($-0.5$ kcal/mol by the additivity procedure$^6$) and the IP estimated to be 8.2 eV, 0.1 eV greater than the adiabatic IP of cyclohexadiene (estimated to be 0.15 eV lower than its vertical IP$^7$). The vertical IP of 2-cyclohexen-1-one$^8$ is 0.1 eV greater than the vertical IP of cyclohexene$^7$.


R. D. Bowen and D. H. Williams, Org. Mass Spectrom., 12, 453 (1977) have proposed this mechanism for double bond migration in alkene radical cations.


Ref. 3, p. 299.

The additivity value for C-(H)(O)(C)(C) was estimated to be $-5.6$ kcal/mol, assuming its value to be greater than the value of $-7.2$ kcal/mol for C-(H)(O)(C) by the same amount that the value of $-6.5$ kcal/mol for C-(H)(O)(C) is greater than the value of $-8.1$ kcal/mol for C-(H)(O)(C). The group additivity value for C-(C)(H)$_2$ is assumed to be the same as C-(C)(H)$_2$, and thus C-(0*)(C*)(C)H is assumed to be the same as C-(0*)(C)H.


The group additivity value for C-(0*)(O)(C)(H) was estimated to be $-1.3$ kcal/mol assuming that the difference between C-(0*)(C)(H) and C-(0*)(O)(C)(H) is the same as the difference between C-(O)(C)H and C-(0*)(C)H. By convention, C-(0*)(O)(C*)(H) was assumed to have the same value as C-(0*)(O)(C)(H), (see last sentence, ref. 12).
(15) Ref. 3, pp. 73 and 275.

(16) The IP of $\text{HOCH}_2\text{CH}_2^+$ has been found by calculation to be 0.11 eV greater than the IP of $\text{CH}_2^+$; see L. Radom, J. A. Pople, and P. von R. Schleyer, J. Amer. Chem. Soc. 94, 5935 (1972). The IP of $\text{CH}_2\text{CH}_2^+$ is approximately 8.35 eV; see F. P. Lossing and G. P. Semeluk, Can. J. Chem. 48, 955 (1970) for their value and literature values.


(18) G. Hvistendahl and D. H. Williams, Ibid. 97, 3097 (1975).

(19) Because the transition state level for the first reaction was revised to 236 kcal/mol$^{20}$ from 227 kcal/mol$^{18}$ the transition state level for this reaction should be revised from 208 kcal/mol$^{18}$ to 217 kcal/mol. The same internal standard was used. The $\Delta H_f$ of the cation, $\text{CH}_2\text{CH}=\text{O}^+\text{CH}_3$, was determined from the daughter ion$^{18}$ and not the metastable ion. A later measurement of the $\Delta H_f$ of this cation gives a value of 132 kcal/mol$^{21}$. Thus, the barrier should be $>85$ kcal/mol.


(22) The $\Delta H_f$ of the unprotonated diradical was estimated to be 40 kcal/mol.$^6$ The proton affinity of this diradical was estimated to be the same as the proton affinity of dimethyl ether.$^{10}$

(23) The $\Delta H_f$ of the unprotonated diradical was estimated to be 30 kcal/mol.$^6$ The proton affinity of this diradical was estimated to be the same as the proton affinity of methylethylether.$^{10}$

(24) The diradical intermediate in the first system was considered to be unlikely because there were no ions characteristic of protonated oxirane.$^{18}$ However, there should be discrimination against an intermediate which has a more ordered transition state than dissociation.

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