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Publication Date

1979-02-01

Submitted to the Journal of American
Chemical Society

LBL-8773 e. 2
Preprint

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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 $\Delta H_f^\ddagger$'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 $\Delta H_f^\ddagger$'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 $\pm$ 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 $\rightleftharpoons$ acetaldehyde, $\text{H}_2\text{C}=\overset{+}{\text{O}}\text{CH}_3 \rightleftharpoons \text{H}_3\overset{+}{\text{C}}=\text{O}=\text{CH}_2$, and $\text{CH}_3\text{CH}=\overset{+}{\text{O}}\text{CH}_3 \rightleftharpoons \text{CH}_3\text{CH}_2\overset{+}{\text{O}}=\text{CH}_2$, 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 determined¹ 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

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

The ΔH_f of ion 2 may be estimated from the proton affinity of benzene,¹⁰ which gives a ΔH_f for cyclohexadienylium of 205.4 kcal/mol. The ΔH_f 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 ΔH_f of 2,4-cyclohexadien-1-yl by the additivity procedure.⁶ The ΔH_f of the diradical corresponding to ion 2 can now be calculated to be 64.1 kcal/mol according to the additivity procedure⁶ using a group additivity value of 9.4 kcal/mol for C-(O·) (C) (C_D) (H) and C-(O·) (C·) (C_D) (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) (C_D)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 ΔH_f for ion 2 of 220 kcal/mol.

The difference in the ΔH_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 ~51 kcal/mol.¹³ Although the ΔH_f of the intermediate formed, $+CH_2CH(OH)O\cdot$, if the tautomerism occurred via successive 1,2-H shifts was estimated to be 205 kcal/mol¹³ by

Franklin's group equivalents, this pathway was considered unlikely because the estimated ΔH_f of the intermediate ion was 10 kcal/mol greater than the experimental transition state energy of 195 ± 10 kcal/mol. An estimation

of -3.4 kcal/mol using group additivity values^{6,14} for the ΔH_f of the diradical corresponding to this intermediate ion and an estimated IP of ~ 8.45 eV for this diradical similar to the IP of $\cdot\text{CH}_2\text{CH}_2\text{OH}$ ¹⁶ gives a value of 191 kcal/mol for the ΔH_f of the intermediate ion. This value indicates that the tautomerism via two successive 1,2-H shifts is energetically possible.

The estimated ΔH_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 ΔH_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 $\text{HOCH}_2\text{CH}_2^+$ ¹⁶.

The barrier to the enol-keto tautomerism of an isolated molecule of vinyl alcohol to acetaldehyde has been found by a recent ab initio calculation to be ~ 105 kcal/mol for the symmetry-forbidden suprafacial 1,3-H shift and ~ 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).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, $\cdot\text{CH}_2\text{CH}_2\text{O}\cdot$, $\Delta H_f(\text{est})$ 41.9 kcal/mol, with an additional 2.5 kcal/mol for the 1,2-H shift.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.⁶ Thus the transition state energy for the vinyl alcohol-acetaldehyde tautomerism via two successive 1,2-H shifts is estimated to be ~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 ≤ 83 kcal/mol for $\text{H}_2\text{C}=\text{O}^+\text{CH}_3 \rightleftharpoons \text{CH}_3\text{O}^+=\text{CH}_2$ ¹⁸ and ≥ 85 kcal/mol for $\text{CH}_3\text{CH}=\text{O}^+\text{CH}_3 \rightleftharpoons \text{CH}_3\text{CH}_2\text{O}^+=\text{CH}_2$.^{18,19} The ΔH_f of the intermediate diradical $\cdot\text{CH}_2\text{OHCH}_2\cdot$, via two successive 1,2-H shifts in the first system was estimated to be 217 kcal/mol by the additivity procedure,²² 19 kcal/mol less than the experimental transition state energy^{18,19} which was considered to be an upper limit. A similar estimation for the ΔH_f of the diradical intermediate in the second system, $\text{CH}_3\dot{\text{C}}\text{HOHCH}_2\cdot$, gave a value of 203 kcal/mol,²³ 14 kcal/mol less than the experimental transition state energy.^{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,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.²⁴

Acknowledgment. We thank Dr. A. M. Falick for helpful comments on the manuscript. The work described in this paper was sponsored, in part, by the Office of Health & Environmental Research, Department of Energy, under contract W-7405-eng-48.

References and Notes

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- (15) Ref. 3, pp. 73 and 275.
- (16) The IP of $\text{HOCH}_2\text{CH}_2^\bullet$ has been found by calculation to be 0.11 eV greater than the IP of ${}^2\text{CH}_2\text{CH}_2^\bullet$; see L. Radom, J. A. Pople and P. von R. Schleyer, *J. Amer. Chem. Soc.* **94**, 5935 (1972). The IP of $\text{CH}_3\text{CH}_2^\bullet$ 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.
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- (22) The ΔH_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 ΔH_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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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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