Using the experimentally determined value $f^{\mathrm{d}} = 0.33$ leads to $a = k_2/k_1 = 0.67$ and $A_4/A_0^0 = 0.40$.

It should be noted that the value calculated for A_4/A_0^0 is not highly sensitive to the values used for the coefficients in Scheme V. For example, if statistical corrections are omitted (as in Scheme IV) and f^{d} is again taken as 0.33, $A_4/A_0^0 = 0.46$.

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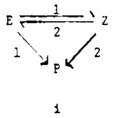

i

On the Mechanism of the Keto-Enol Tautomerism in Radical Cations and Gas-Phase Closed-Shell Systems

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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 ΔH_{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 ΔH_{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. The tautomerism in the closed-shell systems 1-butene $\rightleftharpoons$ 2-butene, vinyl alcohol $\rightleftharpoons$ acetaldehyde, $\mathrm{H_2C{=}O^+CH_3} \rightleftharpoons \mathrm{H_3CO^+{=}CH_2}$, and $\mathrm{CH_3CH{=}O^+CH_3} \rightleftharpoons \mathrm{CH_3CH_2O^+{=}CH_2}$ is discussed in terms of two consecutive 1,2-hydrogen shifts.

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 ion **2**, which should approximate the structure of the intermediate ion in the enol-keto tautomerism by this mechanism.[10,14] The formation of ion **2** would be in accord with the "tight" transition state indicated by the large kinetic shift observed in the decomposition of **1** to give the M − CO ion.[1] The kinetic shift was manifested in a large variation of kinetic energy release with decomposition time.[1]

Energy Estimates and Reaction Mechanism. The ΔH_{f} of ion **2** may be estimated from the proton affinity of benzene,[16]

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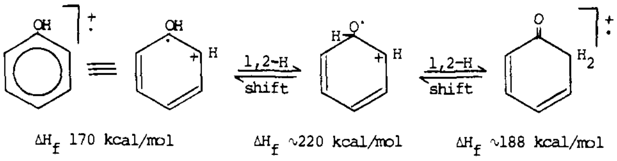
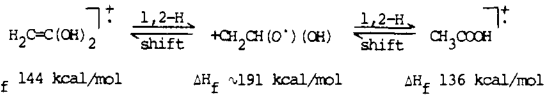


1 2 3

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,[17] and thus the ionization potential (IP) of this radical is 155.4 kcal (6.76 eV). The ΔH_f of the diradical corresponding to ion **2** was calculated to be 64.1 kcal/mol according to the additivity procedure[6] by 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).[18] The ring correction value used was −1.5 kcal/mol, which was obtained from the ΔH_f of 2,4-cyclohexadien-1-yl.[17] By 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. This value compares well with the experimental value of 225 kcal/mol for the transition-state energy.[1]

The barrier to the enol-keto tautomerism of the ionized enol form of acetic acid to ionized acetic acid was found to be ~51 kcal/mol.[19] The mechanism of the tautomerism occurring via two successive 1,2-H shifts was considered unlikely because the ΔH_f of ion **4** was estimated by Franklin's group equivalents



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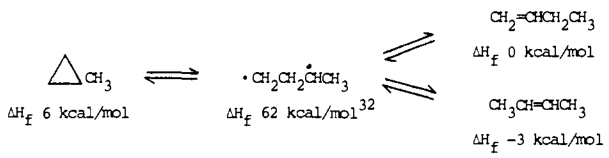
to be 205 kcal/mol[19] which was 10 kcal/mol greater than the experimental transition-state energy of 195 ± 10 kcal/mol. An estimation of −3.4 kcal/mol obtained by using group additivity values[20] for the ΔH_f of the diradical corresponding to **4** and an estimated IP of ~8.45 eV for this diradical similar to the IP of $\cdot CH_2CH_2OH$[22] gives a value of 191 kcal/mol for the ΔH_f of **4**. 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 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 $HOCH_2CH_2^+$.[22] The accuracy of the experimental and calculated data are dependent on the accuracy of the appearance potential (AP) measurements and the ΔH_f's of the radicals. The proton affinity scale, which is based on the ΔH_f of 169 kcal/mol for the *tert*-butyl cation, has been suggested to give values for the ions 4-8 kcal/mol too high.[23] If the recent IP of 6.58 eV[24] and the ΔH_f of 8.4 kcal/mol[25] for the *tert*-butyl radical are used, the ΔH_f of the *tert*-butyl cation is 160 kcal/mol. Thus, the calculated ΔH_f of ions 2 and 4 may be high by 9 kcal/mol.[26] On the other hand, the experimental barriers may also be high by approximately this amount. In addition, the derived additivity values for C-(O·)(C·)(C_d)(H) and C-(O·)(O)(C·)(H) may be high by 2-4 kcal/mol, because the value for C-(O·)$(C)_2$(H) appears to be high by 2-4 kcal/mol.[27]

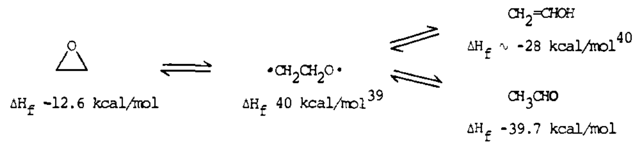
Related Reactions. Comparisons of the barriers in these radical cations have been made[1,19] with the barriers to the thermal uncatalyzed 1,3-H shift in closed shell systems. However, as Woodward and Hoffmann have stated, thermal sigmatropic 1,3 shifts proceed with such high activation energies that the energy surface for concerted reaction cannot be far from that for stepwise processes.[30] Therefore, several examples will be discussed in terms of two successive 1,2-H shifts.

Recently, a study of the pyrolysis of 1-butene at low concentrations indicated that at least 50% of the 2-butene production was via a molecular rearrangement with an activation energy of ~76 kcal/mol.[31] The transition-state energy for this rearrangement via two successive 1,2-H shifts should be similar to that of the structural isomerization of methylcyclopropane



to 1- and 2-butenes which has been considered to proceed via a diradical intermediate.[6] The experimental E_a for the structural isomerization is 64 kcal/mol, in good agreement with the estimate of 63 kcal/mol, which includes an activation energy for the 1,2-H shift from the diradical intermediate.[6b,32] Therefore, the E_a for the rearrangement of 1-butene to 2-butene via two successive 1,2-H shifts would be 69 kcal/mol in fair agreement with the experimental value.[34]

An analogous scheme for the tautomerism of vinyl alcohol to acetaldehyde would indicate an $E_a \geq 72$ kcal/mol based on the experimental E_a for the structural isomerization of oxirane



to acetaldehyde of 57 kcal/mol.[38] The E_a of 4.4 kcal/mol for the 1,2-H shift from the diradical to acetaldehyde was expected to be this amount[39] based on the 80 kcal/mol exothermicity of the reaction. The E_a is 7 kcal/mol for the 1,2-H shift from the trimethylene diradical to propene and the exothermicity, 66 kcal/mol.[41] Thus, the E_a for the 1,2-H shift from the diradical to vinyl alcohol would be ~6 kcal/mol based on the ~71 kcal/mol[42] exothermicity of the reaction, and the E_a of the structural isomerization of oxirane to vinyl alcohol would be ~59 kcal/mol. The E_a for the tautomerism of vinyl alcohol to acetaldehyde via two successive 1,2-H shifts would be ~74 kcal/mol, obtained by using the calculated value[40] for the ΔH_f of vinyl alcohol.

Ab initio calculations of the E_a for the symmetry-forbidden suprafacial 1,3-H shift in propene and vinyl alcohol indicate an E_a of 93 kcal/mol for the 1,3-H shift in propene and 95 kcal/mol for the 1,3-H shift in vinyl alcohol.[40] These values are considerably higher than the values indicated by the biradical mechanism.

The rearrangement in another closed-shell system was attributed to a symmetry-forbidden 1,3-H shift: $CH_3CH{=}O^+CH_3 \rightleftharpoons CH_3CH_2O^+{=}CH_2$.[44] The experimental E_a was found to be a minimum of 58 kcal/mol giving a transition-state energy (TSE) of 208 kcal/mol.[44] The ΔH_f of the intermediate ion, $CH_3\dot{C}HO^+HCH_2\cdot$, which would be formed via two successive 1,2-H shifts, is estimated to be ~201 kcal/mol[46] based on the proton affinity of methyl ethyl ether. The additional E_a for the 1,2-H shift from the intermediate ion to the product ion is estimated to be ~9 kcal/mol[50] giving a TSE of ~210 kcal/mol. This value may be high by 9 kcal/mol as discussed above for ions **2** and **4**. If so, the estimated TSE would be ~201 kcal/mol. The experimental TSE may not be high by very much because the authors later revised the maximum TSE for the 1,3-H shift in $CH_2{=}O^+CH_3$ from 227[44] to 236 kcal/mol.[51] Also, their value for the ΔH_f of

$CH_2{=}O^+CH_3$ was 13 kcal/mol lower[44] than the recent value of 157 kcal/mol.[45]

The experimental TSE for the 1,3-H shift in $CH_2{=}O^+CH_3$ was recently found to be 210 ±7 kcal/mol by the ICR method.[52] If this shift occurs via two successive 1,2-H shifts the estimated ΔH_f of the intermediate ion formed, $\cdot CH_2O^+\text{-}CH_2\cdot$,[53] would be 215 kcal/mol based on the proton affinity of dimethyl ether.[54] An additional E_a of ~9 kcal/mol for the 1,2-H shift from the diradical intermediate would give a TSE of 224 kcal/mol, clearly greater than the experimental TSE.[55] However, the E_a for the 1,2-H shift from the diradical intermediate may be less than 9 kcal/mol. This value is based on the Polanyi relation for the 1,2-H shift in neutral diradicals,[50] and thus there may be different constants in the equation for cation diradicals. Because there are no experimental values to determine these constants, the E_a for the 1,2-H shift is uncertain. As noted,[10] the E_a for the 1,2-H shift from the intermediate ion in radical cations is assumed to be small. Also, the ΔH_f of the intermediate ion is based on the bond dissociation energy (BDE) of the C—H bond in dimethyl ether.[47] If this BDE is high by 2 kcal/mol,[56] the ΔH_f of the intermediate ion would be high by 4 kcal/mol. These changes in the ΔH_f of the intermediate ion and the E_a for the 1,2-H shift from the intermediate ion would also apply to the previous example.

If allowance is made in the last two examples for the uncertainty regarding the E_a for the 1,2-H shift from the intermediate ions as well as the ΔH_f's of these intermediate ions, all the experimental E_a's are consistent with the mechanism of two successive 1,2-H shifts. If the concerted mechanism were operating, the experimental E_a's should have been at least 3 kcal/mol less than the transition-state energies predicted for the two-step mechanism.[37] Thus, the 1,3-H shift in these examples is not obviously concerted. The E_a for the suprafacial, symmetry-forbidden, 1,3-H shift would be equal to or greater than the E_a for the shift via two consecutive 1,2-H shifts. The transition state for the concerted shift would be almost as tight[40] as for the shift via the two-step mechanism.

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(17) Ref 3, p 299.
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(26) A recent value for the PA of ethylene, 166.4 kcal/mol (Y. H. Li, *Diss. Abstr. Int. B*, **37**, 2276 (1976), and ref 16) gives $\Delta H_f(C_2H_5^+) = 213$ kcal/mol. If this value is high by 9 kcal/mol, then the $\Delta H_f(C_2H_5^+)$ should be 204 kcal/mol, which is 15 kcal/mol less than the accepted value of 219 kcal/mol[22] on which the ΔH_f of ion 4 is based. Thus, the ΔH_f of ion 4 may be 15 kcal/mol less than the calculated value of 191 kcal/mol.
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(29) K. Janousek, A. H. Zimmerman, K. J. Reed, and J. I. Brauman, *J. Am. Chem. Soc.*, **100**, 6142 (1978), found the bond strengths to be ~2 kcal/mol less than accepted values.
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(31) D. R. Powers and W. H. Corcoran, *Prepr, Div. Pet. Chem., Am. Chem. Soc.*, **20**, 208 (1975).
(32) The ΔH_f of this diradical is calculated to be 58 kcal/mol according to additivity values.[8a] However, recent data on the ΔH_f of alkyl radicals[28,33] indicates a ΔH_f of 62 kcal/mol.
(33) R. M. Marshall and N. D. Page, *Int. J. Chem. Kinet.*, **11**, 199 (1979).
(34) In the pyrolysis of 1-butene, the competitive reaction to propenyl and methyl radicals has $E_a = 74.5$ kcal/mol and $\log A = 16.0$[31]; rate constant at 575° $= 6.3 \times 10^{-4}\ s^{-1}$. Assuming $\Delta S^{\ddagger} = 0$ for 1-butene $\rightleftharpoons$ 2-butene,[35] $\log A$ was calculated to be 13.7 at 575 °C and the rate constant $8 \times 10^{-5}\ s^{-1}$ for $E_a = 69$ kcal/mol. From the rate constants, the proportions of products due to cleavage (each propenyl and methyl radical reacts with one molecule of 1-butene) to product due to rearrangement is 24:1 in good agreement with the experimental distribution. If the rearrangement were concerted, the E_a would be at least 3 kcal/mol less[37] and the rate constant $5 \times 10^{-4}\ s^{-1}$. The amount of 2-butene due to rearrangement would be ~21%, much greater than the ~5% which could be attributed to molecular rearrangement.
(35) $\Delta S^{\ddagger} = 0$ for propene → cyclopropane from $S^\circ = 64$ eu for the transition state and $S^\circ = 64$ eu for propene.[36]
(36) Ref 6b, p 15, for $\Delta S^{\ddagger} = 7$ eu for cyclopropane → propene, and ref 6b, p 223, for $S^\circ = 57$ eu for cyclopropane and $S^\circ = 64$ eu for propene.
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(39) S. W. Benson, *J. Chem. Phys.*, **40**, 105 (1964). The ΔH_f of the diradical was estimated to be 40 kcal/mol in this reference and is consistent with recent data.[27,28]
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(41) These values are based on ΔH_f of 71 kcal/mol for the trimethylene diradical estimated from the recent ΔH_f of the *n*-propyl radical.[28]
(42) The ΔH_f of vinyl alcohol was calculated[40] to be 12 kcal/mol greater than the ΔH_f of acetaldehyde. However, experimental data on other enols[43] indicates a ΔH_f of −31 kcal/mol for vinyl alcohol.

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(46) The ΔH_f of the unprotonated diradical was estimated to be 28 kcal/mol from the bond dissociation energy (BDE = 93.3 kcal/mol) of the C–H bond of dimethyl ether[47] and the BDE of ~91 kcal/mol for the methylene C–H bond of methyl ethyl ether which was estimated to be lower than the BDE of the C–H bond of dimethyl ether by the same amount that the BDE of the methylene C–H bond of ethanol[48] is less than the BDE of the C–H bond of methanol.[49] The proton affinity of the diradical was estimated to be the same as the PA of methyl ethyl ether.[16]
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(50) From the Polanyi equation $E_a = C - \alpha(\Delta H^0)$ for exothermic reactions; $C = 19.3$, $\alpha = 0.186$ from the E_a for the 1,2-H shift in $\cdot CH_2CH_2CH_2\cdot$ and $\cdot CH_2CH_2O\cdot$.
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(52) R. van Doorn and N. M. M. Nibbering, *Org. Mass Spectrom.*, **13**, 527 (1978).
(53) This intermediate ion was considered unlikely[44] because there were no ions characteristic of protonated oxirane. However, there should be discrimination against an intermediate which has a more ordered transition state than dissociation.
(54) The ΔH_f of the unprotonated diradical was estimated to be 38 kcal/mol from the BDE of 93.3 kcal/mol for the C–H bond of dimethyl ether.[47] The PA of this diradical was estimated to be the same as the PA of dimethyl ether.[18]
(55) An adjustment for the PA values as discussed for ions 2 and 4 would require an equal adjustment for the experimental TSE, because it is based on the ΔH_f of 157 kcal/mol for $CH_2{=}O^+CH_3$[45] which is relative to the ΔH_f's of ions which have similar ΔH_f's found from PA values.
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Mechanism of Indole–Singlet Oxygen Reactions. Interception of Zwitterionic Intermediates and "Ene" Reaction[1]

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Abstract: The trapping reaction of zwitterionic peroxides formed in singlet oxygen reaction of *N*-methylindoles is described. The zwitterionic peroxide derived from 1,3-dimethylindole (**1**) was intercepted by methanol, ethanol, isopropyl alcohol, and β-methoxyethanol. The trend of the efficiency of the trapping reactions by these alcohols was parallel to that for the interception of zwitterions from tetracyanoethylene and enol ethers by alcohols. It has been shown that the introduction of an electron-withdrawing substituent into the indole ring favors the trapping reaction over the oxidative cleavage of the 2,3 double bond. Thus, the photooxygenation of 1,2,3-trimethyl-5-nitroindole (**7c**), 9-methyl-6-nitro-1,2,3,4-tetrahydrocarbazole (**10a**), and 9-acetyl-1,2,3,4-tetrahydrocarbazole (**10b**) in methanol gave the corresponding trapping products **9**, **11a**, and **11b**, respectively, whereas 1,2,3-trimethylindole (**7a**), 5-methoxy-1,2,3-trimethylindole (**7b**), and 9-methyl-1,2,3,4-tetrahydrocarbazole (**10c**) yielded only the ring cleavage products. Photooxygenation of **7a** in alcohols gave the ring cleavage product **8a** as the major product, whereas in aprotic solvents **7a** produced the ene-type product **13a.** In contrast, photooxygenation of 1,2-dimethyltryptophol (**7e**) gave only the trapping product **16** in both protic and aprotic solvents. The result suggests that a common intermediate for both "ene" and 1,2 cycloaddition is captured intramolecularly by the nucleophilic group of the side chain. The experimental results have been explained by the mechanism involving gauche and cis zwitterions as the intermediates.

Introduction

Electron-rich alkenes such as enamines and enol ethers are known to react readily with singlet oxygen to yield unstable dioxetanes which can subsequently cleave to two carbonyl fragments.[2] The mechanisms of the 1,2 cycloaddition are the subjects of much current controversy, the main question being whether the reactions are concerted or involve intermediates. A symmetry-allowed concerted $[_\pi 2_s + {}_\pi 2_a]$ process has been first proposed for the 1,2 cycloaddition of singlet oxygen to olefins.[2b,3-5] According to the orbital and state correlation diagrams, the $[_\pi 2_s + {}_\pi 2_s]$ approach should be forbidden.[2b] However, this process might occur in the case of alkenes with particularly low ionization potentials.[2b,3,4] Stepwise 1,2 cycloaddition might occur via short-lived intermediates such as perepoxides,[2b,8] zwitterions,[4,7] or 1,4 biradicals.[9] An electron transfer mechanism involving a radical cation and superoxide radical anion pair has also been proposed for the 1,2 cycloaddition of singlet oxygen to enamines.[10] Recent theoretical studies have reported that zwitterionic intermediates should be important in the reaction of singlet oxygen with electron-rich olefins,[4,7] whereas Harding and Goddard have proposed by GVB–CI calculations the mechanism involving a 1,4 biradical stabilized by an anomeric effect for the hydroperoxidation of methoxy-substituted olefins.[9b]

Considerable experimental work has been done in order to elucidate the mechanism of the 1,2 cycloaddition. Bartlett and Schaap[5] were the first to propose a concerted mechanism or one involving short-lived, stereochemically stable intermediates, based on the experimental observations, namely, the lack of a solvent effect on the rate of photooxygenation of *cis*-diethoxyethylene and the absence of stereochemical leakage during the photooxygenation in a polar solvent. On the other hand, we proposed over 10 years ago a zwitterionic precursor in the photooxygenation of highly electron-rich enamines such as fully N-alkylated uric acids.[11] Thereafter, there have been reported several examples in which products might be most reasonably explained in terms of zwitterions.[12] Recently, Conia et al.[13] and Jefford[14] have proposed a zwitterionic intermediate in explaining the high regioselectivity in the singlet oxygenation of cyclopropylethylenes. Zwitterionic intermediates are also postulated to play an important role in the reaction of triplet molecular oxygen with ketenes[15] or strained acetylenes.[16] However, these results do not provide conclusive evidence for the zwitterionic precursors. A chemical confirmation by in-

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